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(57) Abstract

Disclosed is the use of enzyme containing solid detergent compositions that can be used to remove food soil from typically food or foodstuff related manufacturing equipment or processing surfaces without the use of corrosives such as chlorine. In particular, the invention relates to the removal of milk proteins from dairy processing equipment. The invention further relates to the use of said composition in a clean-in-place system in which electrical conductivity is used to control the concentration of detergent within the system. Although various enzymes can be used, the preferred embodiment of the invention uses proteases to assist in removing the milk proteins from the processing equipment. The protease is stabilized by including sodium borate, sucrose, milk or the combination thereof in the use solution. The sodium borate also functions as an aid to solidification, as a buffering agent and also functions as an alkalinity source. It is the sodium borate which permits the use of a high level of electrolyte for conductivity control.

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SOLID BLOCK ENZYMATIC CLEANING WITH ELECTROLYTIC CONTROL FOR CLEAN-IN-PLACE SYSTEMS

Field of the Invention

The invention relates to enzyme containing solid detergent compositions that can be used to remove food soil from typically food or foodstuff related manufacturing equipment or processing surfaces. The invention relates to the use of said composition in a clean-in-place system. Further, the invention relates to the use of electrical conductivity to control the concentration of enzyme cleaner during cleaning operations.

Background of the Invention

Periodic cleaning and sanitizing in the food process industry is a regimen mandated by law and rigorously practiced to maintain the exceptionally high standards of food hygiene and shelf-life expected by today's consumer. Residual food soil, left on food contact equipment surfaces for prolonged periods, can harbor and nourish growth of opportunistic pathogen and food spoilage microorganisms that can contaminate foodstuffs processed in close proximity to the residual soil. Insuring protection of the consumer, against potential health hazards associated with food borne pathogens and toxins and, maintaining the flavor, nutritional value and quality of the foodstuff, requires diligent cleaning and soil removal from any surfaces of which contact the food product directly or are associated with the processing environment.

The term "cleaning", in the context of the care and maintenance of food preparation surfaces and equipment, refers to the treatment given all food product contact surfaces following each period of operation to substantially remove food soil residues including any residue that can harbor or nourish any harmful microorganism. Freedom from such residues, however, does not indicate perfectly clean equipment. Large populations of microorganisms may exist on food process surfaces even after visually successful cleaning. The concept of cleanliness as applied in the food process plant is a continuum wherein absolute cleanliness is the

ideal goal always strived for; but, in practice, the cleanliness achieved is of lesser degree.

The term "sanitizing" refers to an antimicrobial treatment applied to all surfaces after the cleaning is effected that reduces the microbial population to safe levels. The critical objective of a cleaning and sanitizing treatment program, in any food process industry, is the reduction of microorganism populations on targeted surfaces to safe levels as established by public health ordinances or proven acceptable by practice. This effect is termed a "sanitized surface" or "sanitization". A sanitized surface is, by Environmental Protection Agency (EPA) regulation, a consequence of both an initial cleaning treatment followed with a sanitizing treatment. A sanitizing treatment applied to a cleaned food contact surface must result in a reduction in population of at least 99.999% reduction (5 log order reduction) for a given microorganism. Sanitizing treatment is defined by "Germicidal and Detergent Sanitizing Action of Disinfectants", Official Methods of Analysis of the Association of Official Analytical Chemists, paragraph 960.09 and applicable sections, 15th Edition, 1990 (EPA Guideline 91-2). Sanitizing treatments applied to non-food contact surfaces in a food process facility must cause 99.9% reduction (3 log order reduction) for given microorganisms as defined by the "Non-Food Contact Sanitizer Method, Sanitizer Test" (for inanimate, non-food contact surfaces), created from EPA DIS/TSS-10, 07 January '82. Although it is beyond the scope of this invention to discuss the chemistry of sanitizing treatments, the microbiological efficacy of these treatments is significantly reduced if the surface is not clean prior to sanitizing. The presence of residual food soil can inhibit sanitizing treatments by acting as a physical barrier which shields microorganisms lying within the soil layer from the microbicide or by inactivating sanitizing treatments by direct chemical interaction which deactivates the killing mechanism of the microbicide. Thus, the more perishable the food, the more effective the cleaning treatment must be.

The technology of cleaning in the food process industry has traditionally been empirical. The need for cleaning treatments existed before a fundamental understanding of soil deposition and removal mechanism was developed. Because of food quality and public health pressures, the food processing industry has attained

a high standard of practical cleanliness and sanitation. This has not been achieved without great expense, and there is considerable interest in more efficient and less costly technology. As knowledge about soils, the function of cleaning chemicals, and the effects of cleaning procedures increased and, as improvements in plant design and food processing equipment become evident, the cost effectiveness and capability of cleaning treatments, i.e. cleaning products and procedures, to remove final traces of residue have methodically improved. The consequence for the food process industry and for the public is progressively higher standards.

The search for ever more efficient and cost effective cleaning treatments, coupled with increasing demand for user friendly and environmentally compatible cleaning chemicals, has fostered a growing number of investigations which have significantly augmented understanding of soil deposition and removal processes by theoretical treatise rather than empirical experimentation. Many modes of improvement can occur including improved chemical or formulation efficacy and process simplification, etc. See, for example, "Theory and Practice of Hard-Surface Cleaning", Jennings, W.G., Advances in Food Research, Vol. 14, pp. 325-455 (1965); or, "Forces in Detergency", Harris, J.C., Soap and Chemical Specialties, Vol. 37 (5), Part I, pp. 68-71 and 125; Vol. 37 (6), Part II, pp. 50-52; Vol. 37 (7), Part III, pp. 53-55; Vol. 37 (8), Part IV, pp. 61-62, 104, 106; Part V, pp. 61-64; (1961) or "Physico-chemical aspects of hard-surface cleaning. Soil removal mechanisms", Koopal, L.K., Neth. Milk Dairy J., 39, pp. 127-154 (1985). Such studies confirm that soil deposition on a surface and the sequential transitions of soil adherence to the surface (adsorption), soil removal from the surface and soil suspension in a cleaning/solution, can be described in terms of well established, generally accepted concepts of colloidal and surface chemistry. The significance of this association is that predictive tools now exist which assist the design of chemical cleaning compounds optimized for specific soils or formulated to overcome other deficiencies in the cleaning program.

These precepts suggest that a clean surface is difficult to maintain, that energy is released (entropy is increased) during soil deposition which favors physicochemical stability, i.e. a soiled surface is nature's preferred or more stable condition. To reverse this process and clean the surface, energy must necessarily be

supplied. In normal practice, this energy takes the form of mechanical and thermal energies carried to the soiled surface. Chemical (detergent) additives to the cleaning solution (usually water) reduce the amount of energy required to reverse the energetically favored soiling process. Thus, the definition of detergent (Definition of the Word "Detergent", Bourne, M.C. and Jennings, W.G., The Journal of the American Oil Chemists' Society, 40, p. 212 (1963)) is "any substance that either alone or in a mixture reduces the work requirement of a cleaning process". Simply, detergents are used because they make cleaning easier. It follows that the word "detergency" is "then understood to mean cleaning or removal of soil from a substrate by a liquid medium."

Soil removal cannot be considered a spontaneous process because soil removal kinetics require a finite period. The longer the cleaning solution is in contact with the deposited soil, the more soil is removed - to a practical limit. Final traces of soil become increasingly difficult to remove. In the last phase of the soil removal process, cleaning involves overcoming the very strong adhesive force between soil and substrate surface, rather than the weaker cohesive soil-soil forces; and, an equilibrium state is eventually attained when soil redeposition occurs at the same rate as soil removal. Thus the major operational parameters of a cleaning treatment in a food process facility are mechanical work level, solution temperature, detergent composition and concentration, and contact time. Of course other variables such as equipment surface characteristics; soil composition, concentration, and condition; and water composition effect the cleaning treatment. However, these factors cannot be controlled and consequently must be compensated for as required.

The food process industry has come to rely more on detergent efficiency to compensate for design or operational deficiencies in their cleaning programs. This is not to suggest that the industry has not addressed these factors; indeed, cleaning processes have changed considerably during recent years because of technological advances in food processing equipment and development of specialized cleaning equipment. Modern food processing industries have revolutionized their clean-up procedures through cleaning-in-place (CIP) and automation.

A major challenge of detergent development for the food process industry is the successful removal of soils that are resistant to conventional treatment and the

elimination of chemicals that are not compatible with food processing. One such soil is protein, and one such chemical is chlorine or chlorine yielding compounds, which can be incorporated into detergent compounds or added separately to cleaning programs for protein removal.

Protein soil residues, often called protein films, occur in all food processing industries but the problem is greatest for the dairy industry, including milk and milk products producers, because dairy products are among the most perishable of major foodstuffs and any soil residues have serious quality consequences. That protein soil residues are common in the fluid milk and milk by-products industry, including dairy farms, is no surprise because protein constitutes approximately 27% of natural milk solids, ("Milk Components and Their Characteristics", Harper, W.J., in Diary Technology and Engineering (editors Harper. W. J. and Hall, C. W.) p. 18-19. The AVI Publishing Company, Westport, 1976).

Proteins are biomolecules which occur in the cells, tissues and biological fluids of all living organisms. Proteins range in molecular weight from about 6000 (single protein chain) to several millions (protein chain complexes) and can simplistically be described as polyamides composed of covalently linked alpha amino acids. Of over 100 naturally occurring amino acids, only 20 are utilized in protein biosynthesis - their number and sequential order characterizing each protein. The covalent bond that joins amino acids together in proteins is called a peptide bond and is formed by reaction between the alpha amino ($-NH_3^+$) protonated group of one amino acid and the alpha carboxyl ($-COO^-$) group of another. These reactions occur in solution; and, alpha amino ($-NH_2$) groups and alpha carboxyl (-COOH) groups are ionized at physiological pH with the protonated amino group bearing a positive charge and the deprotonated carboxyl group a negative charge.

Polypeptides alone do not make a biologically functional protein. A unique conformation or three-dimensional structure also must exist, which is determined by interactions between a polypeptide and its aqueous environment, and driven by such fundamental forces as ionic or electrostatic interactions; hydrophobic interactions; hydrogen and covalent bonding; and charge transfer interactions. The complex three-dimensional structure of the protein macromolecule is that conformation which maximizes stability and minimizes the necessary energy to maintain. In fact, four

levels of structure influence a protein's structure; three being intramolecular and existing in single polypeptide chains, and the fourth being intermolecular associations within a multi-chained molecule. Principles of protein structure are available in modern biochemistry textbooks, for example: Biochemistry, Armstrong, F. B., 3rd edition, Oxford University Press, New York, 1989; or Physical Biochemistry, Freifelder, D., 2nd edition, W. H. Eruman Company, San Francisco, 1982; or Principles of Protein Structure, Schultz, G. E. and Schumer, R. H., Springer-Verlag, Berlin, 1979.

Protein interactions with surfaces have been studied for decades, with early focus on blood-plasma-serum applications and more recent emphasis in the so-called biocompatibility-biomaterials field or medical device implants. This work characterized the solid surface-protein solution interface and developed a range of new concepts and new experimental tools for research. Two comprehensive reviews of this literature are: "Principles of Protein Adsorption", in Surface and Interfacial Aspects of Biomedical Polymers, Andrade, J.D., (editor Andrade, J.D.), Vol. 2, pp. 1-80, Plenum Press, New York, 1985; and "Protein Adsorption and Materials Biocompatibility: A Tutorial Review and Suggested Hypotheses", Andrade, J.D. and Hlady, V., Advances in Polymer Science, Vol. 79, pp. 1-63, Springer-Verlag Berlin Heidelberg, 1986.

A growing source of protein adsorption information is now in literature, specifically dealing with soils. Studies have established that the same intrinsic interactions and associations within the protein molecule responsible for three-dimensional structure also attract and bind proteins to surfaces. Because of their size and complex structure, proteins contain heterogeneous modules consisting of electrically charged (both negative and positive) regions, hydrophobic regions, and hydrophilic polar regions, analogous in character to similar areas on food processing equipment surfaces having trace soil residues. The protein can thus interact with the hard surface in a variety of different ways, depending on the particular orientation exposed to the surface, the number of binding sites, and overall binding energies.

Because biological fluids such as milk are complex mixtures, the kinetics of the protein adsorption process are confused by concurrent events occurring at interfacial surfaces within the bulk solution and at the equipment surfaces.

Temperature, pH, protein populations and concentrations, and presence of other inorganic and organic moieties have effect on rate dynamics. In general, however, there is general agreement that protein adsorption is rapid, reversible, and randomly arranged at fractional surface coverages less than 50%; and, the rate is mass transport controlled, i.e. all adsorption and desorption processes depend on transport of bulk solute to and from the interface. As coverage exceeds 50%, surface ordering develops, and given sufficient contact time, adsorbed proteins undergo conformational and orientational changes to optimize interfacial interactions and system stability. Proteins less optimally adsorbed undergo desorption or exchange by larger proteins having more binding sites. The process rate becomes surface reaction limited (mass action controlled). With increasing residence time, protein adsorption becomes irreversible.

Several representative articles describing food soil deposition studies are: "Fouling of Heating Surfaces - Chemical Reaction Fouling Due to Milk", Sandu, C. and Lund, D., in Fouling and Cleaning in Food Processing (editors Lund, D., Plett, E., and Sandu, C.), pp. 122-167, University of Wisconsin-Madison Extension Duplicating, Madison, 1985; and, "Model Studies of Food Fouling", Gotham, S.M., Fryer, P.J., and Pritchard, A.M., in Fouling and Cleaning in Food Processing (editors Kessler, H. B. and Lund, D. B.), pp. 1-13, Druckerei Walch, Augsburg, 1989; and "Fouling of Milk Proteins and Salts - Reduction of Fouling by Technological Measures", Kessler, H.B., Ibid., pp. 37-45.

Theory suggests that irreversible protein adsorption begins as a tenacious monomolecular layer tightly bound by protein-surface interfacial forces. Polylayers and protein then deposit with repeated exposure, bound by protein-protein cohesive forces, each layer being progressively weaker in binding energy as the distance increases from the original substrate surface. Experimental observation and practical experience in milk process facilities confirm that several soil-clean cycles generally occur before protein films become visually discernible on surfaces, manifested by a light blue-brown to dark blue-black discoloration. Precise analytical confirmation can be made by a simple surface qualitative test utilizing Coomassie Brilliant Blue dye, which exists in two color forms -- red and blue, the red rapidly converting to blue upon contact with protein. This dye-protein complex has a high extinction

coefficient effecting great sensitivity in both qualitative and quantitative measurement of protein (see "The Use of Coomassie Brilliant Blue G250 Perchloric Acid Solution for Staining in Electrophoresis and Isoelectric Focusing on Polyacrylamide Gels"; Reisner, A.H., Nemes, P. and Bucholtz, C.; Analytical Biochemistry, Vol. 64, pp. 509-516 (1975); and, "A Rapid and Sensitive Method for the Quantitation of Microgram Quantities of Protein Utilizing the Principle of Protein-Dye Binding"; Bradford, M.M., Analytical Biochemistry, Vol. 72, pp. 248-254 (1976)).

As additional layers of protein deposit one upon another, a maximum thickness is likely reached above which cohesive protein-protein binding forces can be overcome by the mechanical, thermal, and detersive energies delivered to the soil by the cleaning program. This would explain results of elution experiments wherein surfaces previously soiled with milk and cleaned are then subjected to a second cleaning process having higher mechanical, thermal and detersive energies which can strip additional protein. However, practical observations suggest that protein films remain even at extremes of cleaning program conditions. A mechanism different than preferential displacement from absorptive sites is needed for protein film removal.

Researchers conducting soil removal experiments in the 1950's with the then new concept of recirculation cleaning (latter termed clean-in-place or CIP to encompass different methodologies) observed the occurrence of protein films on milk process equipment surfaces. Subsequently, the addition of hypochlorite to CIP alkaline detergent compounds was found to help remove protein film; and, this technology has been employed to-date by suppliers of cleaning compounds to the general food process industry. (For example, see "Effect of Added Hypochlorite on Detergent Activity of Alkaline Solutions in Recirculation Cleaning", MacGregor, D.R., Elliker, P.R., and Richardson, G.A., Jnl. of Milk & Food Technology, Vol. 17, pp. 136-138 (1954); "Further Studies on In-Place Cleaning", Kaufmann, O.W., Andrews, R.H., and Tracy, P.H., Journal of Dairy Science, Vol. 38, No. 4, 371-379 (1955); and, "Formation and Removal of an Iridescent Discoloration in Cleaned-In-Place Pipelines", Kaufmann, O.W. and Tracy, P.H., Ibid., Vol. 42, pp. 1883-1885 (1959).

Chlorine degrades protein by oxidative cleavage and hydrolysis of the peptide bond, which breaks apart large protein molecules into smaller peptide chains. The conformational structure of the protein disintegrates, dramatically lowering the binding energies, and effecting desorption from the surface, followed by solubilization or suspension into the cleaning solution.

The use of chlorinated detergent solutions in the food process industry is not without problems. Corrosion is a constant concern, as is degradation of polymeric gaskets, hoses, and appliances. Practice indicates that available chlorine concentrations must initially be at least 75, and preferably, 100 ppm for optimum protein film removal. At concentrations of available chlorine less than 50 ppm, protein soil build-up is enhanced by formation of insoluble, adhesive chloro-proteins (see "Cleanability of Milk-Filmed Stainless Steel by Chlorinated Detergent Solutions", Jensen, J.M., Journal of Dairy Science, Vol. 53, No. 2, pp. 248-251 (1970). Chlorine concentrations are not easy to maintain or analytically discern in detersive solutions. The dissipation of available chlorine by soil residues has been well established; and, chlorine can form unstable chloramino derivatives with proteins which titrate as available chlorine. The effectiveness of chlorine on protein soil removal diminishes as solution temperature and pH decrease -- lower temperatures affecting reaction rate, and lower pH favoring chlorinated additional moieties.

These problems associated with the use and applications of chlorine release agents in the food process industry have been known and tolerated for decades. Chlorine has improved cleaning efficiency, and improved sanitation resulting in improved product quality. No safe and effective, lower cost alternative has been advanced by the detergent manufacturers.

However, a new issue may force change upon both the food process industry and the detergent manufacturers -- the growing public concern over the health and environmental impacts of chlorine and organochlorines. Whatever the merits of the scientific evidence regarding carcinogenicity, there is little argument that organohalogen compounds are persistent and bioaccumulative; and that many of these compounds pose greater non-cancer health effects -- endocrine, immune, and neurological problems -- principally in the offspring of exposed humans and

wildlife, at extremely low exposure levels. It is, therefore, prudent for the food process industry and their detergent suppliers to refocus on finding alternatives to the use of chlorine release agents in cleaning compositions.

A substantial need exists for a non-chlorine, protein film stripping agent for detergent compositions having applications in the food process industry, and having the versatility to remedy the problems heretofore described and presently unresolved.

Although enzymes were discovered in the early 1830's and their importance prompted intensive study by biochemists, public record of research into applications of enzymes in detergents first occurred in 1915 when German Patent No. 283,923 issued (May 4) to O. Rohm, founder of Rohm & Haas for application of pancreatic enzymes in laundry wash products. E. Jaag of the Swiss firm Gebrueder Schnyder developed this enzyme detergent concept further over the course of 30 years work; and, in 1959, introduced to market a laundry product, Bio 40, which contained a bacterial protease having considerable advantages over pancreatic trypsin. However, this bacterial protease was still not sufficiently stable at normal use pH of 9-10 and had marginal activity upon typical stains. It took several more years of research, until the mid 1960's, before bacterial alkaline proteases were commercial which had all of the necessary pH stability and soil reactivity characteristics for detergent applications.

Although use of enzymes in cleaning compositions did exist prior (see for example U.S. Pat. No. 1,882,279 to Frelinghuysen issued October 11, 1932), large scale commercial enzyme containing laundry detergents first appeared in the United States in test market during 1966. Since that time, a large, but narrowly focused number of patents have been issued and reference articles published which disclose detergent compositions containing alkaline protease or enzyme class and subclass admixtures generally of proteases, carbohydrases and esterases. The vast majority of these patents target enzyme applications in consumer laundry pre-soak or wash cycle detergent compositions and consumer automatic dishwashing detergents. Close scrutiny of this patent library discloses the evolution of formula development in these product categories from simple powders containing alkaline protease (see for example U.S. Pat. No. 3,451,935 to Roald et al., issued June 24, 1969) to more

complex granular compositions containing multiple enzymes (see for example U.S. Pat. No. 3,519,570 to McCarty issued July 7, 1970); to liquid compositions containing enzymes.

The progression from dry to liquid detergent compositions containing enzymes was a natural consequence of inherent problems with dry powder forms. Enzyme powders or granulates tended to segregate in these mechanical mixtures resulting in non-uniform, and hence undependable, product in use. Precautions had to be taken with packaging and in storage to protect the product from humidity which caused enzyme degradation. Dry powdered compositions are not as conveniently suited as liquids for rapid solubility or miscibility in cold and tepid waters nor functional as direct application products to soiled surfaces. For these reasons and for expanded applications, it became desirable to have liquid enzyme compositions.

Economic as well as processing considerations suggest the use of water in liquid enzyme compositions. However, there are also inherent problems in formulating enzymes into aqueous compositions. Enzymes generally denature or degrade in an aqueous medium resulting in the serious reduction or complete loss of enzyme activity. This instability results from at least two mechanisms. Enzymes have three-dimensional protein structure which can be physically or chemically changed by other solution ingredients, such as surfactants and builders, causing loss of catalytic effect. Alternately when protease is present in the composition, the protease will cause proteolytic digestion of the other enzymes if they are not proteases; or of itself via a process called autolysis.

Examples in the prior art have attempted to deal with these aqueous induced enzyme stability problems by minimizing water content (see U.S. Pat. No. 3,697,451 to Mausner et al. issued October 10, 1972) or altogether eliminating water from the liquid enzyme containing composition (see U.S. Pat. No. 4,753,748 to Lailem et al. issued June 28, 1988). As disclosed in Mausner et al. and apparent from Lailem et al., water is advantageous to dissolve the enzyme(s) and other water soluble ingredients, such as builders, and effectively carry or couple them into the non-aqueous liquid detergent vehicle to effect a homogenous, isotropic liquid which will not otherwise phase separate.

In order to market an aqueous enzyme composition, the enzyme must be stabilized so that it will retain its functional activity for prolonged periods of (shelf-life or storage) time. If a stabilized enzyme system is not employed, an excess of enzyme is generally required to compensate for expected loss. However, enzymes are expensive and are in fact the most costly ingredients in a commercial detergent even though they are present in relatively minor amounts. Thus, it is no surprise that methods of stabilizing enzyme-containing, aqueous, liquid detergent compositions are extensively described in the patent literature. (See, Guilbert, U.S. Pat. No. 4,238,345).

Whereas the stabilizers used in liquid aqueous enzyme detergent compositions inhibit enzyme deactivation by chemical intervention, the literature also includes enzyme compositions which contain high percentages of water, but the water or the enzyme or both are immobilized; or otherwise physically separated to prevent hydrolytic interaction. For example of an aqueous enzyme encapsulate formed by extrusion, see U.S. Pat. No. 4,087,368 to Borrello issued May 2, 1978. For example of a gel-like aqueous based enzyme detergent, see U.S. Patent No. 5,064,553 to Dixit et al. issued November 12, 1991. For example of a dual component, two-package composition wherein the enzyme is separated from the alkalies, builders and sequestrants, see U.S. Pat. No. 4,243,543 to Guilbert et al. issued January 6, 1981.

In 1985, a paper authored by D. R. Kane and N.E. Middlemiss entitled "Cleaning Chemicals - State of the Knowledge in 1985" (in Fouling and Cleaning in Food Processing; editors Lund, D. Plett, E., and Sandu, C.; pp. 312-335, University of Wisconsin - Madison Extension Duplicating, Madison, 1985) was delivered to the Second International Conference of Fouling and Cleaning in Food Processing. This paper emphasized CIP (clean-in-place) cleaning in the dairy industry. Within the text of this paper, the authors conclude that enzyme use in the food cleaning industry is not widespread for several reasons including enzyme instability at high pH and over time, enzyme and enzyme stabilizer cost, concern about residual enzyme and adverse effect on foodstuff quality, enzyme incompatibility with chlorine, slow enzyme reactivity necessitating long cleaning cycle times, and no commercial justification.

The present invention addresses and resolves these issues and problems and provides a usful control method for using the cleaner composition. The art does contain prior disclosure of enzyme containing detergent compositions having application on food process equipment. U.S. Pat. No. 4,169,817 to Weber issued October 2, 1979 discloses a liquid cleaning composition containing detergent builders, surfactants, enzyme and stabilizing agent. The compositions claimed by Weber may be employed as a laundry detergent, a laundry pre-soak, or as a general purpose cleaner for dairy and cheese making processing equipment. The detergent solution of Weber generally has a pH in the range of 7.0 to 11.0. The aforementioned prior teaching embodies high foam surfactants and fails to provide detergents which can be utilized in CIP cleaning systems.

U.S. Pat. No. 4,212,761 to Ciaccio issued July 15, 1980 discloses a neat or use solution composition containing a ratio of sodium carbonate and sodium bicarbonate, a surfactant, an alkaline protease, and optionally sodium tripolyphosphate. The detergent solution of Ciaccio is used for cleaning dairy equipment including clean-in-place methods. The pH of the use solution in Ciaccio ranges from 8.5 to 11. In Ciaccio, no working examples of detergent concentrate embodiments are disclosed. Ciaccio only asserts that the desirable detergent form would be as a premixed particulate not a solid block. From the ingredient ranges discussed, it becomes obvious to one skilled in the art that such compositions would be too wet, sticky, and mull-like in practice to be readily commercialized.

U.S. Pat. Nos. 4,238,345 and 4,243,543 to Guilbert issued January 6, 1981 teach a liquid two-part cleaning system for clean-in-place applications wherein one part is a concentrate which consists essentially of a proteolytic enzyme, enzyme stabilizers, surfactant and water; with the second concentrated part comprised of alkalies, builders, sequestrants and water. When both parts were blended at use dilution in Guilbert, the pH of this use solution was typically 11 or 12.

U.S. Pat. No. 5,064,561 to Rouillard issued November 12, 1991 discloses a two-part cleaning system for use in clean-in-place facilities. Part one is a liquid concentrate consisting of a highly alkaline material (NaOH), defoamer, solubilizer or emulsifier, sequestrant and water. Part two is a liquid concentrate containing an enzyme which is a protease generally present as a liquid or as a slurry within a non-

aqueous carrier which is ordinarily an alcohol, surfactant, polyol or mixture thereof. The use solution of Rouillard generally has a pH of about 9.5 to about 10.5.

Rouillard teaches the use of high alkaline materials; and, paradoxically, the optional use of buffers to stabilize the pH of the composition. Rouillard's invention discloses compositions wherein unstable aqueous mixtures of inorganic salts and organic defoamer are necessarily coupled by inclusion of a solubilizer or emulsifier to maintain an isotropic liquid concentrate. Rouillard further teaches that the defoamer may not always be required if a liquid (the assumption of term is "aqueous, stabilized") form of the enzyme is used in the second concentrate. This disclosure would seem to result from the use of Esperase 8.0 SL identified as a useful source of enzyme in the practice of the invention and utilized in working examples. Additional detail indicates Esperase 8.0 SL is a proteolytic enzyme suspended in Tergitol 15-S-9, a high foam surfactant -- hence the need for a defoamer and for a solubilizer or emulsifier. Rouillard still further discloses that proteolytic enzyme (Esperase 8.0 SL) of an by itself does not clean as effectively as a high alkaline, chlorinated detergent unless mixed with its cooperative alkaline concentrate.

As discussed in WO 97/02753, issued to Olsen, cleaning in place (CIP) involves circulating non-foaming or low foaming detergents through process equipment in the assembled state. A typical CIP sequence may consist of the following five stages (see Hygiene for Management by R.A. Sprenger, 5th Edition, p. 135):

1. Prerinse with cold water to remove gross soil;
2. Detergent circulation to remove residual adhering debris and scale;
3. Intermediate rinse with cold water to remove all traces of detergent;
4. Disinfectant circulation to destroy remaining microorganisms; and
5. Final rinse with cold water to remove all traces of disinfectants.

U.S. Patent No. 4,858,449, issued to Lehn teaches the use of dispensers which dispense solid alkaline chemicals used in cleaning processes which control the quantity of chemical dispensed by periodically measuring the conductivity of the

concentrated chemical solution. This invention periodically measures the conductivity of the consorted solution in order to determine the amount of solution which has been dispensed. Various chemicals can be used as long as the solutions conductivity can be correlated with its concentration.

U.S. Patent No. 4,211,517, issued to Schmid discloses the use of measuring pH in order to determine the conductivity.

U.S. Patent No. 4,845,965, issued to Copeland et al discloses the use of a conductivity sensor which is used for controlling the dispensing of multiple alkaline cleaning solutions to one or more laundry machines using preferably a single delivery system. The conductivity sensor is used to monitor the concentration of the concentrated detergent solution. U.S. Patent No. 4,826,661, also issued to Copeland et al teaches the preparation of a concentrated cleaning solution by contacting a solid block cleaning composition with the dissolving liquid.

U.S. Patent No. 4,690,305, issued to Copeland et al discloses a washed chemical dispenser for dispensing a concentrated alkaline chemical solution by contacting a solid block with an aqueous liquid.

WO 97/02753, issued to Olsen, relates to an enzymatic method of clean in place self processing equipment, in particular, slaughter house process equipment. The invention discloses a method of clean in place process equipment comprising circulating a solution comprising a protease and a lipase for a sufficient period of time to permit action of the enzymes.

WO 96/41859, issued to Nielsen, relates to a liquid composition, in particular to a liquid detergent composition, comprising an enzyme and an improved enzyme stabilizer. The enzyme stabilizers in this patent generally are phenyl boronic acid derivatives.

WO 93/21299, issued to Marshall, et al relates to a liquid automatic dishwashing detergent composition which is substantially free of chlorine bleach and silicate. The automatic dishwashing composition contains enzyme, an enzyme stabilizing system and detergent surfactant or detergent builder.

WO 97/07190, issued to Rouillard, teaches the use of portion packed powdered low alkaline enzymatic detergents for cleaning milk lines at a dairy installation.

Summary of the Invention

This invention discloses formulations comprising enzyme, borate, carbohydrate, etc. in a solid form. Further methods of manufacture and methods of use for compositional embodiments having application as detergents in the food process industry are disclosed. We have also discovered a method that controls enzyme concentration with conductivity. Said compositions are used in cleaning food soiled surfaces. The materials are made in concentrated form. The diluted concentrate when delivered to the targeted surfaces will provide cleaning. The concentrated product is a solid. The concentrate products being manufactured by any number of solid blending methods known to the art inclusive of casting, pour-molding, compressions-molding, extrusion-molding or similar shape - packaging operations. The preferred embodiment comprises the use of extrusion to create the solid block detergent. Said products being designed for clean-in-place (CIP) cleaning regimens in food process industries such as dairy plant and farm; fluid milk and processed milk by-product. More specifically, the present invention describes detergent compositions generally containing enzymes, surfactants and sequestrants.

The claimed compositions eliminate the need for high alkaline builders, axillary defoamers, corrosion inhibitors, and chlorine release agents. Accordingly the claimed compositions are safer to use and resulting effluent is friendly to the environment. When used, the claimed composition will continue to clean soiled food process equipment surfaces equal to or better than present, conventional chlorinated - high alkaline detergents.

We have also found preferred methods of cleaning protein containing food processing units. In the preferred methods of the invention, the food processing units having at least some minimal film residue derived from the protein containing food product, is contacted with a protease containing detergent composition of the invention. Optionally, prior to contacting the food processing surface with the detergent, the unit can be prerinsed with an aqueous rinse composition to remove gross food soil. The protein residue on the food processing unit is contacted with a detergent of the invention for a sufficient period of time to remove the protein film. Any protease enzyme residue remaining on the surfaces of the unit or otherwise

within the food processing unit, can be denatured using a variety of techniques. The food processing unit can be heated with a heat source comprising steam, hot water, etc. above the denaturing temperature of the protease enzyme. Typically, temperatures required range from about 60-90°C, preferably about 60-80°C. Further, the residual protease enzyme remaining in the food processing unit can be denatured by exposing the enzyme to an extreme pH. Typically, a pH greater than about 10, preferably greater than about 11 (alkaline pH) or less than 5, preferably less than about 4 (acid pH) is sufficient to denature the enzyme.

Additionally, the protease can be denatured by exposing any residual protease enzyme to the effects of an oxidizing agent. A variety of known oxidizing agents that also have the benefit of acting as a food acceptable sanitizer include aqueous hydrogen peroxide, aqueous ozone containing compositions, aqueous peroxy acid compositions wherein the peroxy acid comprises a per C_{1-24} monocarboxylic or dicarboxylic acid composition. Additionally, hypochlorite, iodophors and interhalogen complexes (ICl, ClBr, etc.) can be used to denature the enzyme if used in accordance with accepted procedures.

Denatured enzyme remaining in the system after the denaturing step can have little or no effect on any proteinaceous food. The resulting product quality is unchanged. Preferred foods treated in food processing units having a denaturing step following the cleaning step include milk and dairy products, beer and other fermented malt beverages, puddings, soups, yogurt, or any other liquid, thickened liquid, or semisolid protein containing food material.

The objectives of this product invention are thus to:

1. provide the food process industry and operations concerned about environmental hygiene with a low alkaline, non-chlorine detergent clean-in-place cleaning system;
2. satisfy a commercial need for cost effective, user friendly, less environmentally intrusive detergents;
3. and resolve objections to the use of detersive enzymes for cleaning in food process environments which are sensitive to enzyme residuals by teaching cooperative cleaning and sanitizing programs which assure complete deactivation of enzyme prior to food contact.

Brief Description of the Drawings

Figure 1 is a graphical representation of stability of residual enzyme activity data for various test formulations.

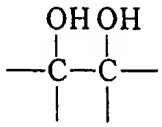
Detailed Description of the Invention

The invention comprises a use dilution, use-solution composition having exceptional detergency properties when applied as a cleaning treatment to food soiled equipment surfaces and having particular cleaning efficiency upon tenacious protein films. Preferred embodiments of the invention provide cleaning performance superior to conventional high alkaline, chlorine containing detergents and is directed especially to the diary industry in which milk proteins are involved. The present invention generally comprises in a low foaming solid or solid block formulation free of an alkaline metal hydroxide or a source of active chlorine:

1. an enzyme or enzyme mixture
2. an alkali metal borate composition that acts as an enzyme stabilizing system
3. a carbohydrate compound
4. a sequestrant
5. water.

A preferred concentrate embodiment of this invention is a detergent system which comprises a stabilized solid block detergent which is made by solidifying a liquid detergent premix with borate alone or together with other solidifying agents. The premix contains a liquid protease enzyme source, an optional surfactant and a sequestrant. The other said solidifying agents are selected from carbonates, bicarbonates, sulfates and urea. The enzyme is stabilized by a borate salt, a carbohydrate composition or a combination thereof. An important aspect is the use of borate for multiple functions: stabilization of the enzyme, solidification, alkalinity source and buffering agent (with a pK_a of 9.1).

We have found that the solid enzyme containing detergents stabilized by the stabilizing compounds of the invention can be further enhanced using a borate stabilizing material. The combination of an alkali metal borate with the vicinal hydrocarbon stabilizer compositions of the invention produce enhanced stability. Boric acid chemistry, like many other chemistries is complex and contains many simple and complex compounds. Mixtures of $B(OH)_3$ and $B(OH)_4^{-1}$ appear in classic buffer systems depending on pH. Sodium borate, potassium borate, disodium tetraborate, disodium tetraborate pentahydrate, disodium tetraborate decahydrate, etc. can be used in the stabilized materials of the invention. We have found that borate compounds alone and combined with a carbohydrate compounds having vicinal hydroxyl groups can act as stabilizing agents for the enzyme materials. The alkali metal salts of boric acid or more complex borates (oligomers of boric acid including both linear and cyclic borate materials) can be used. Preferred materials are species such as $Na_2O{\cdot}B_4O_7{\cdot}XH_2O$, disodium tetraborate pentahydrate, disodium tetraborate decahydrate, anhydrous borax, sodium pentaborate decahydrate, sodium metaborate octahydrate, sodium metaborate tetrahydrate and others can be prepared. Borax decahydrate and borax pentahydrate are produced by extraction from dry-lake brines and other natural sources. The enzyme stabilizer compositions of the invention can also include an organic C_4 compound with at least one vicinal hydroxide group corresponding to the following formula:



wherein the empty bonds correspond to carbon, oxygen, hydrogen, sulfur, nitrogen or other common atoms in available stabilizer compounds. The simplest examples are glycerin derivatives such as glycerin lower alkyl monoesters and ethers including glyceryl monostearate, glyceryl monooleate, glyceryl-monoethyl ether, glyceryl-diethyl ether, etc. 2,3-dihydroxybutyraldehyde, and other C_{4+} organic compounds having vicinal hydroxyls. One class of preferred stabilizers are the monosaccharides including aldotetrose, aldopentose, aldohexose, aldoheptose, aldooctose, ketotetrose, ketopentose, ketohexose, etc. compounds. Such compounds include erythrose, ribose, glucose, mannose, galactose, isomers and derivatives thereof and other

similar monosaccharides. Additionally, disaccharides compounds including sucrose, lactose, cellobiose, maltose are useful.

The present invention related to a CIP system in which a stabilized enzyme is used to remove milk proteins from milk processing equipment. Further, the present invention relates to the use of electrolytic control to regulate the concentration of detergent within the system.

The benefits of the present invention include an ability to clean with enzymes. Consequently, the cleaning solution is less alkaline and uses less water. Because no chlorine is used. there are fewer problems with corrosiveness.

Enzymes

Enzymes are important and essential components of biological systems, their function being to catalyze and facilitate organic and inorganic reactions. For example, enzymes are essential to metabolic reactions occurring in animal and plant life.

The enzymes of this invention are simple proteins or conjugated proteins produced by living organisms and functioning as biochemical catalysts which, in detergent technology, degrade or alter one or more types of soil residues encountered on food process equipment surfaces thus removing the soil or making the soil more removable by the detergent-cleaning system. Both degradation and alteration of soil residues improve detergency by reducing the physicochemical forces which bind the soil to the surface being cleaned, i.e. the soil becomes more water soluble.

As defined in the art, enzymes are referred to as simple proteins when they require only their protein structures for catalytic activity. Enzymes are described as conjugated proteins if they require a non-protein component for activity, termed cofactor, which is a metal or an organic biomolecule often referred to as a coenzyme. Cofactors are not involved in the catalytic events of enzyme function. Rather, their role seems to be one of maintaining the enzyme in an active configuration. As used herein, enzyme activity refers to the ability of an enzyme to perform the desired catalytic function of soil degradation or alteration; and, enzyme stability pertains to the ability of an enzyme to remain or to be maintained in the active state.

Enzymes are extremely effective catalysts. In practice, very small amounts will accelerate the rate of soil degradation and soil alteration reactions without themselves being consumed in the process. Enzymes also have substrate (soil) specificity which determines the breadth of its catalytic effect. Some enzymes interact with only one specific substrate molecule (absolute specificity); whereas, other enzymes have broad specificity and catalyze reactions on a family of structurally similar molecules (group specificity).

Enzymes exhibit catalytic activity by virtue of three general characteristics: the formation of a noncovalent complex with the substrate, substrate specificity, and catalytic rate. Many compounds may bind to an enzyme, but only certain types will lead to subsequent reaction. The later are called substrates and satisfy the particular enzyme specificity requirement. Materials that bind but do not thereupon chemically react can affect the enzymatic reaction either in a positive or negative way. For example, unreacted species called inhibitors interrupt enzymatic activity.

Enzymes which degrade or alter one or more types of soil, i.e. augment or aid the removal of soils from surfaces to be cleaned, are identified and can be grouped into six major classes on the basis of the types of chemical reactions which they catalyze in such degradation and alteration processes. These classes are (1) oxidoreductase; (2) transferase; (3) hydrolase; (4) lyase; (5) isomerase; and (6) ligase.

Several enzymes may fit into more than one class. A valuable reference on enzymes is "Industrial Enzymes", Scott, D., in Kirk-Othmer Encyclopedia of Chemical Technology, 3rd Edition, (editors Grayson, M. and EcKroth, D.) Vol. 9, pp. 173-224, John Wiley & Sons, New York, 1980.

In summary, the oxidoreductases, hydrolases, lyases and ligases degrade soil residues thus removing the soil or making the soil more removable; and, transferases and isomerases alter soil residues with same effect. Of these enzyme classes, the hydrolases (including esterase, carbohydrase or protease) are particularly preferred for the present invention.

The hydrolases catalyze the addition of water to the soil with which they interact and generally cause a degradation or breakdown of that soil residue. This breakdown of soil residue is of particular and practical importance in detergent

applications because soils adhering to surfaces are loosened and removed or rendered more easily removed by detersive action. Thus, hydrolases are the most preferred class of enzymes for use in cleaning compositions. Preferred hydrolases are esterases, carbohydrases, and proteases. The most preferred hydrolase sub-class for the present invention is the proteases.

The proteases catalyze the hydrolysis of the peptide bond linkage of amino acid polymers including peptides, polypeptides, proteins and related substances - generally protein complexes - such as casein which contains carbohydrate (glyco group) and phosphorus as integral parts of the protein and exists as distinct globular particles held together by calcium phosphate; or such as milk globulin which can be thought of as protein and lipid sandwiches that comprise the milk fat globule membrane. Proteases thus cleave complex, macromolecular protein structures present in soil residues into simpler short chain molecules which are, of themselves, more readily desorbed from surfaces, solubilized or otherwise more easily removed by detersive solutions containing said proteases.

Proteases, a sub-class of hydrolases, are further divided into three distinct subgroups which are grouped by the pH optima (i.e. optimum enzyme activity over a certain pH range). These three subgroups are the alkaline, neutral and acids proteases. These proteases can be derived from vegetable, animal or microorganism origin; but, preferably are of the latter origin which includes yeasts, molds and bacteria. More preferred are serine active, alkaline proteolytic enzymes of bacterial origin. Particularly preferred for embodiment in this invention are bacterial, serine active, alkaline proteolytic enzymes obtained from alkalophilic strains of Bacillus, especially from Bacillus subtilis and Bacillus licheniformis. Purified or non-purified forms of these enzymes may be used. Proteolytic enzymes produced by chemically or genetically modified mutants are herein included by definition as are close structural enzyme variants. These alkaline proteases are generally neither inhibited by metal chelating agents (sequestrants) and thiol poisons nor activated by metal ions or reducing agents. They all have relatively broad substrate specificities, are inhibited by diisopropylfluorophosphate (DFP), are all endopeptidases, generally have molecular weights in the range of 20,000 to 40,000, and are active in the pH

ranges of from about 6 to about 12; and, in the temperature range of from about 20°C to about 80°C.

Examples of suitable commercially available alkaline proteases are Alcalase®, Savinase®, and Esperase® -- all of Novo Industri AS, Denmark; Purafect® of Genencor International; Maxacal®, Maxapem® and Maxatase® -- all of Gist-Brocase International NV, Netherlands; Optimase® and Opticlean® of Solvay Enzymes, USA and so on.

Commercial alkaline proteases are obtainable in liquid or dried form, are sold as raw aqueous solutions or in assorted purified, processed and compounded forms, and are comprised of about 2% to about 80% by weight active enzyme generally in combination with stabilizers, buffers, cofactors, impurities and inert vehicles. The actual active enzyme content depends upon the method of manufacture and is not critical, assuming the detergent solution has the desired enzymatic activity. The particular enzyme chosen for use in the process and products of this invention depends upon the conditions of final utility, including the physical product form, use pH, use temperature, and soil types to be degraded or altered. The enzyme can be chosen to provide optimum activity and stability for any given set of utility conditions. For example, Purafect® is a preferred alkaline protease for use in detergent compositions of this invention having application in lower temperature cleaning programs -- from about 30°C to about 65°C; whereas, Esperase® is the alkaline protease of choice for higher temperature detersive solutions, from about 50°C to about 85°C.

In preferred embodiments of this invention, the amount of commercial alkaline protease composite present in the final use-dilution, use-solution ranges from about 0.001% (10 ppm) by weight of detersive solution to about 0.02% (200 ppm) by weight of solution of the commercial enzyme product, which typically contains 5-10 percent of active enzyme.

Whereas establishing the percentage by weight of commercial alkaline protease required is of practical convenience for manufacturing embodiments of the present teaching, variance in commercial protease concentrates and in-situ environmental additive and negative effects upon protease activity require a more

discerning analytical technique for protease assay to quantify enzyme activity and establish correlations to soil residue removal performance and to enzyme stability within the preferred embodiment; and, if a concentrate, to use-dilution solutions. The activity of the alkaline proteases of the present invention are readily expressed in terms of activity units -- more specifically, Kilo-Novo Protease Units (KNPU) which are azocasein assay activity units well known to the art. A more detailed discussion of the azocasein assay procedure can be found in the publication entitled "The Use of Azoalbumin as a Substrate in the Colorimetric Determination of Peptic and Tryptic Activity", Tomarelli, R.M., Charney, J., and Harding, M.L., J. Lab. Clin. Chem. 34, 428 (1949), incorporated herein by reference.

In preferred embodiments of the present invention, the activity of proteases present in the use-solution ranges from about 1 x 10^{-5} KNPU/gm solution to about 4 x 10^{-3} KNPU/gm solution.

Naturally, mixtures of different proteolytic enzymes may be incorporated into this invention. While various specific enzymes have been described above, it is to be understood that any protease which can confer the desired proteolytic activity to the composition may be used and this embodiment of this invention is not limited in any way by specific choice of proteolytic enzyme.

In addition to proteases, it is also to be understood, and one skilled in the art will see from the above enumeration, that other enzymes which are well known in the art may also be used with the composition of the invention. Included are other hydrolases such as esterases, carboxylases and the like; and, other enzyme classes.

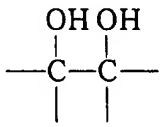
Further, in order to enhance its stability, the enzyme or enzyme admixture may be incorporated into various non-liquid embodiments of the present invention as a coated, encapsulated, agglomerated, prilled or marumerized form.

Enzyme Stabilizing System

The enzyme stabilizing system of the present invention consists of sodium borate, sucrose. milk or a combination thereof.

It seems obvious to conclude that this enzyme stabilizing system would therefor provide some degree of stabilizing effect to enzyme activity at all levels of free and bound waters existing in a liquid enzyme detergent composition, typically from about 1% to about 99% by weight of water.

We have found that incorporation of the preferred enzyme stabilizing system has pronounced beneficial effect upon alkaline protease cleaning performance, i.e. enhanced protein film removal, in use-dilution solutions. Normally, employed for shelf-life maintenance of enzyme activity within the product concentrate, none of the art discloses, teaches or suggests that enzyme stabilizing systems make any contribution to or have any expected cooperative action with enzyme activity or manifested cleaning performance improvement within detersive, use-dilution solution environments. The enzyme stabilizer compositions of the invention include an organic C_{4+} compound with at least one vicinal hydroxide group corresponding to the following formula:



wherein the empty bonds correspond to carbon, oxygen, hydrogen, sulfur, nitrogen or other common atoms in available stabilizer compounds. The simplest examples are glycerin derivatives such as glycerin lower alkyl monoesters and ethers including glyceryl monostearate, glyceryl monooleate, glyceryl-monoethyl ether, glyceryl-diethyl ether, etc. 2,3-dihydroxybutyraldehyde, and other C_{4+} organic compounds having vicinal hydroxyls. One class of preferred reversion inhibitors are the monosaccharides including aldotetrose, aldopentose, aldohexose, aldoheptose, aldooctose, ketotetrose, ketopentose, ketohexose, etc. compounds. Such compounds include erythrose, ribose, glucose, mannose, galactose, isomers and derivatives thereof and other similar monosaccharides. Additionally, disaccharides compounds including sucrose, lactose, cellobiose, maltose are useful. The stabilizer, solidification, etc. agent of the invention can include an alkali metal borate.

We have also found that borate compounds and borate compounds, optionally combined with carbohydrate compounds having vicinal hydroxyl groups, can act as stabilizing agents for the enzyme materials. The alkali metal salts of boric acid or more complex borates (oligomers of boric acid including both linear and cyclic borate materials) can be used. Preferred materials are species such as $Na_2B_4O_7 \cdot XH_2O$; $Na_2O \cdot B_4O_6 \cdot XH_2O$ or $Na_2O \cdot B_2O_3 \cdot XH_2O$, etc., wherein X is about 0 to 12, including disodium tetraborate decahydrate, disodium tetraborate pentahydrate, anhydrous borax, sodium pentaborate decahydrate, sodium metaborate octahydrate, sodium metaborate tetrahydrate and others can be prepared. Borax (anhydrous), borax decahydrate and borax pentahydrate are produced by extraction and drying from dry-lake brines and other natural sources.

Furthermore, none of the art discloses, teaches, or suggests that such enzyme stabilizing systems will profoundly demonstrate this synergistic, cooperative effect at high temperatures otherwise destructive to enzymes or rendering them thermolabile.

Surfactant

The surfactant or surfactant admixture of the present invention can be selected from water soluble or water dispersible nonionic, semi-polar nonionic, anionic, cationic, amphoteric, or zwitterionic surface-active agents; or any combination thereof.

The particular surfactant or surfactant mixture chosen for use in the process and products of this invention depends upon the conditions of final utility, including method of manufacture, physical product form, use pH, use temperature, foam control, and soil type.

Surfactants incorporated into the present invention must be enzyme compatible and free of enzymatically reactive species. For example, when proteases and amylases are employed, the surfactant should be free of peptide and glycosidic bonds respectively. Care should be taken in including cationic surfactants because some reportedly decrease enzyme effectiveness.

The preferred surfactant system of the invention is selected from nonionic or anionic species of surface-active agents, or mixtures of each or both types. Nonionic

and anionic surfactants offer diverse and comprehensive commercial selection, low price; and, most important, excellent detersive effect -- meaning surface wetting, soil penetration, soil removal from the surface being cleaned, and soil suspension in the detergent solution. This preference does not teach exclusion of utility for cationics, or for that sub-class of nonionic entitled semi-polar nonionics, or for those surface-active agents which are characterized by persistent cationic and anionic double ion behavior, thus differing from classical amphoteric, and which are classified as zwitterionic surfactants.

One skilled in the art will understand that inclusion of cationic, semi-polar nonionic, or zwitterionic surfactants; or, mixtures thereof will impart beneficial and/or differentiating utility to various embodiments of the present invention. As example. foam stabilization for detersive compositions designed to be foamed onto equipment or environmental floor, wall and ceiling surfaces; or, gel development for products dispensed as a clinging thin gel onto soiled surfaces; or, for antimicrobial preservation; or, for corrosion prevention -- and so forth.

The most preferred surfactant system of the present invention is selected from nonionic or anionic surface-active agents, or mixtures of each or both types which impart low foam to the use-dilution, use solution of the detergent composition during application. Preferably, the surfactant or the individual surfactants participating within the surfactant mixture are of themselves low foaming within normal use concentrations and within expected operational application parameters of the detergent composition and cleaning program. In practice, however, there is advantage to blending low foaming surfactants with higher foaming surfactants because the latter often impart superior detersive properties to the detergent composition. Mixtures of low foam and high foam nonionics and mixtures of low foam nonionics and high foam anionics can be useful in the present invention if the foam profile of the combination is low foaming at normal use conditions. Thus high foaming nonionics and anionics can be judiciously employed without departing from the spirit of this invention.

Particularly preferred concentrate embodiments of this invention are designed for clean-in-place (CIP) cleaning systems within food process facilities; and, most particularly for dairy farm and fluid milk and milk by-product producers.

Foam is a major concern in these highly agitated, pump recirculation systems during the cleaning program. Excessive foam reduces flow rate, cavitates recirculation pumps, inhibits detersive solution contact with soiled surfaces, and prolongs drainage. Such occurrences during CIP operations adversely affect cleaning performance and sanitizing efficiencies.

Low foaming is therefore a descriptive detergent characteristic broadly defined as a quantity of foam which does not manifest any of the problems enumerated above when the detergent is incorporated into the cleaning program of a CIP system. Because no foam is the ideal, the issue becomes that of determining what is the maximum level or quantity of foam which can be tolerated within the CIP system without causing observable mechanical or detersive disruption; and, then commercializing only formulas having foam profiles at least below this maximum; but, more practically, significantly below this maximum for assurance of optimum detersive performance and CIP system operation.

Acceptable foam levels in CIP systems have been empirically determined in practice by trial and error. Obviously, commercial products exist today which meet the low foam profile needs of CIP operation. It is therefore, a relatively straightforward task to employ such commercial products as standards for comparison and to establish laboratory foam evaluation devices and test methods which simulate, if not duplicate, CIP program conditions, i.e. agitation, temperature, and concentration parameters.

In practice, the present invention permits incorporation of high concentrations of surfactant as compared to conventional chlorinated, high alkaline CIP and COP cleaners. Certain preferred surfactant or surfactant mixtures of the invention are not generally physically compatible nor chemically stable with the alkalis and chlorine of convention. This major differentiation from the art necessitates not only careful foam profile analysis of surfactants being included into compositions of the invention; but, also demands critical scrutiny of their detersive properties of soil removal and suspension. The present invention relies upon the surfactant system for gross soil removal from equipment surfaces and for soil suspension in the detersive solution. Soil suspension is as important a surfactant property in CIP detersive systems as soil removal to prevent soil redeposition on

cleaned surfaces during recirculation and later re-use in CIP systems which save and re-employ the same detersive solution again for several cleaning cycles.

Generally, the concentration of surfactant or surfactant mixture useful in use-dilution, use solutions of the present invention ranges from about 0.002% (20 ppm) by weight to about 0.1% (1000 ppm) by weight, preferably from about 0.005% (50 ppm) by weight to about 0.075% (750 ppm) by weight, and most preferably from about 0.008% (80 ppm) by weight to about 0.05% (500 ppm) by weight.

The concentration of surfactant or surfactant mixture useful in the most preferred concentrated embodiment of the present invention ranges from about 5% by weight to about 75% by weight of the total formula weight percent of the enzyme containing composition.

A typical listing of the classes and species of surfactants useful herein appears in U.S. Pat. No. 3,664,961 issued May 23, 1972, to Norris, incorporated herein by reference. Nonionic Surfactants, edited by Schick, M.J., Vol. 1 of the Surfactant Science Series, Marcel Dekker, Inc., New York, 1983 is an excellent reference on the wide variety of nonionic compounds generally employed in the practice of the present invention. Nonionic surfactants useful in the invention are generally characterized by the presence of an organic hydrophobic group and an organic hydrophilic group and are typically produced by the condensation of an organic aliphatic, alkyl aromatic or polyoxyalkylene hydrophobic compound with a hydrophilic alkaline oxide moiety which in common practice is ethylene oxide or a polyhydration product thereof, polyethylene glycol. Practically any hydrophobic compound having a hydroxyl, carboxyl, amino, or amido group with a reactive hydrogen atom can be condensed with ethylene oxide, or its polyhydration adducts, or its mixtures with alkoxylenes such as propylene oxide to form a nonionic surface-active agent. The length of the hydrophilic polyoxyalkylene moiety which is condensed with any particular hydrophobic compound can be readily adjusted to yield a water dispersible or water soluble compound having the desired degree of balance between hydrophilic and hydrophobic properties. Useful nonionic surfactants in the present invention include:

1. Block polyoxypropylene-polyoxyethylene polymeric compounds based upon propylene glycol, ethylene glycol, glycerol, trimethylolpropane, and

ethylenediamine as the initiator reactive hydrogen compound. Examples of polymeric compounds made from a sequential propoxylation and ethoxylation of initiator are commercially available under the trade name Pluronic® and Tetronic® manufactured by BASF Corp.

Pluronic® compounds are difunctional (two reactive hydrogens) compounds formed by condensing ethylene oxide with a hydrophobic base formed by the addition of propylene oxide to the two hydroxyl groups of propylene glycol. This hydrophobic portion of the molecule weighs from about 1,000 to about 4,000. Ethylene oxide is then added to sandwich this hydrophobe between hydrophilic groups, controlled by length to constitute from about 10% by weight to about 80% by weight of the final molecule.

Tetronic® compounds are tetra-functional block copolymers derived from the sequential addition of propylene oxide and ethylene oxide to ethylenediamine. The molecular weight of the propylene oxide hydrotype ranges from about 500 to about 7,000; and, the hydrophile, ethylene oxide, is added to constitute from about 10% by weight to about 80% by weight of the molecule.

2. Condensation products of one mole of alkyl phenol wherein the alkyl chain, of straight chain or branched chain configuration, or of single or dual alkyl constituent, contains from about 8 to about 18 carbon atoms with from about 3 to about 50 moles of ethylene oxide. The alkyl group can, for example, be represented by diisobutylene, di-amyl, polymerized propylene, iso-octyl, nonyl, and di-nonyl. Examples of commercial compounds of this chemistry are available on the market under the trade name Igepal® manufactured by Rhone-Poulenc and Triton® manufactured by Union Carbide.

3. Condensation products of one mole of a saturated or unsaturated, straight or branched chain alcohol having from about 6 to about 24 carbon atoms with from about 3 to about 50 moles of ethylene oxide. The alcohol moiety can consist of mixtures of alcohols in the above delineated carbon range or it can consist of an alcohol having a specific number of carbon atoms within this range. Examples of like commercial surfactant are available under the trade name Noedol®

manufactured by Shell Chemical Co. and Alfonic® manufactured by Vista Chemical Co.

4. Condensation products of one mole of saturated or unsaturated, straight or branched chain carboxylic acid having from about 8 to about 18 carbon atoms with from about 6 to about 50 moles of ethylene oxide. The acid moiety can consist of mixtures of acids in the above defined carbon atoms range or it can consist of an acid having a specific number of carbon atoms within the range. Examples of commercial compounds of this chemistry are available on the market under the trade name Nopalcol® manufactured by Henkel Corporation and Lipopeg® manufactured by Lipo Chemicals, Inc.

In addition to ethoxylated carboxylic acids, commonly called polyethylene glycol esters, other alkanoic acid esters formed by reaction with glycerides, glycerin, and polyhydric (saccharide or sorbitan/sorbitol) alcohols have application in this invention for specialized embodiments, particularly indirect food additive applications. All of these ester moieties have one or more reactive hydrogen sites on their molecule which can undergo further acylation or ethylene oxide (alkoxide) addition to control the hydrophilicity of these substances. Care must be exercised when adding these fatty ester or acylated carbohydrates to compositions of the present invention containing amylase and/or lipase enzymes because of potential incompatibility.

Low foaming alkoxylated nonionics are preferred although other higher foaming alkoxylated nonionics can be used without departing from the spirit of this invention if used in conjunction with low foaming agents so as to control the foam profile of the mixture within the detergent composition as a whole. Examples of nonionic low foaming surfactants include:

5. Compounds from (1) which are modified, essentially reversed, by adding ethylene oxide to ethylene glycol to provide a hydrophile of designated molecular weight; and, then adding propylene oxide to obtain hydrophobic blocks on the outside (ends) of the molecule. The hydrophobic portion of the molecule weighs from about 1,000 to about 3,100 with the central hydrophile comprising 10% by

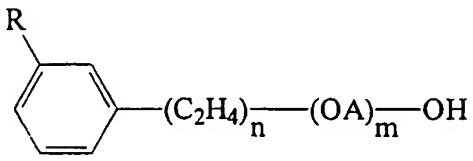
weight to about 80% by weight of the final molecule. These reverse Pluronics® are manufactured by BASF Corporation under the trade name Pluronic® R surfactants.

Likewise, the Tetraonic® R surfactants are produced by BASF Corporation by the sequential addition of ethylene oxide and propylene oxide to ethylenediamine. The hydrophobic portion of the molecule weighs from about 2,100 to about 6,700 with the central hydrophile comprising 10% by weight to 80% by weight of the final molecule.

6. Compounds from groups (1), (2), (3) and (4) which are modified by "capping" or "end blocking" the terminal hydroxy group or groups (of multi-functional moieties) to reduce foaming by reaction with a small hydrophobic molecule such as propylene oxide, butylene oxide, benzyl chloride; and, short chain fatty acids, alcohols or alkyl halides containing from 1 to about 5 carbon atoms; and mixtures thereof. Also included are reactants such as thionyl chloride which convert terminal hydroxy groups to a chloride group. Such modifications to the terminal hydroxy group may lead to all-block, block-heteric, heteric-block or all-heteric nonionics.

7. Additional examples of effective low foaming nonionics include:

The alkylphenoxypolyethoxyalkanols of U.S. Pat No. 2,903,486 issued September 8, 1959 to Brown et al., hereby incorporated by reference, represented by the formula



in which R is an alkyl group of 8 to 9 carbon atoms, A is an alkylene chain of 3 to 4 carbon atoms. n is an integer of 7 to 16, and m is an integer of 1 to 10.

The polyalkylene glycol condensates of U.S. Pat. No. 3,048,548 issued August 7, 1962 to Martin et al., hereby incorporated by reference, having alternating hydrophilic oxyethylene chains and hydrophobic oxypropylene chains where the weight of the terminal hydrophobic chains, the weight of the middle hydrophobic

unit and the weight of the linking hydrophilic units each represent about one-third of the condensate.

The defoaming nonionic surfactants disclosed in U.S. Pat. No. 3,382,178 issued May 7 1968 to Lissant et al., incorporated herein by reference, having the general formula $Z[(OR)_nOH]_z$ wherein Z is alkoxylatable material, R is a radical derived from an alkaline oxide which can be ethylene and propylene and n is an integer from, for example, 10 to 2,000 or more and z is an integer determined by the number of reactive oxyalkylatable groups.

The conjugated polyoxyalkylene compounds described in U.S. Pat. No. 2,677,700, issued May 4, 1954 to Jackson et al., incorporated herein by reference, corresponding to the formula $Y(C_3H_6O)_n(C_2H_4O)_mH$ wherein Y is the residue of organic compound having from about 1 to 6 carbon atoms and one reactive hydrogen atom, n has an average value of at least about 6.4, as determined by hydroxyl number and m has a value such that the oxyethylene portion constitutes about 10% to about 90% by weight of the molecule.

The conjugated polyoxyalkylene compounds described in U.S. Pat. No. 2,674,619, issued April 6, 1954 to Lundsted et al, incorporated herein by reference, having the formula $Y[(C_3H_6O_n(C_2H_4O)_mH]_x$ wherein Y is the residue of an organic compound having from about 2 to 6 carbon atoms and containing x reactive hydrogen atoms in which x has a value of at least about 2, n has a value such that the molecular weight of the polyoxypropylene hydrophobic base is at least about 900 and m has value such that the oxyethylene content of the molecule is from about 10% to about 90% by weight. Compounds falling within the scope of the definition for Y include, for example, propylene glycol, glycerine, pentaerythritol, trimethylolpropane, ethylenediamine and the like. The oxypropylene chains optionally, but advantageously, contain small amounts of ethylene oxide and the oxyethylene chains also optionally, but advantageously, contain small amounts of propylene oxide.

Additional conjugated polyoxyalkylene surface-active agents which are advantageously used in the compositions of this invention correspond to the formula: $P[(C_3H_6O)_n(C_2H_4O)_mH]_x$ wherein P is the residue of an organic compound having from about 8 to 18 carbon atoms and containing x reactive hydrogen atoms in

which x has a value of 1 or 2, n has a value such that the molecular weight of the polyoxyethylene portion is at least about 44 and m has a value such that the oxypropylene content of the molecule is from about 10% to about 90% by weight. In either case the oxypropylene chains may contain optionally, but advantageously, small amounts of ethylene oxide and the oxyethylene chains may contain also optionally, but advantageously, small amounts of propylene oxide.

Examples of especially preferred commercial surfactants are listed in Table II.

Table II

Examples of Preferred Commercial Nonionics

General Structure	Examplesa
AP-$(EO)_x$-$(PO)_y$H	Triton® CF-21 $C_8P(EO)_{9.5}(PO)_5H$
Alcohol-$(EO)_x$-$(PO)_y$H	Sulfonic® JL-80X $C_{9-11}(EO)_9(PO)_{1-2}H$
Alcohol-$(PO)_x$-$(EO)_y$H	Poly-Tergent® SL-=42 $C_{8-10}(PO)_3(EO)_5H$
Alcohol-$(PO)_x$-$(EO)_y$-$(PO)_2$H	Poly-Tergent ® SLF-18 $C_{8-10}(PO)_{16-17}(EO)_{12}(PO)_{1-2}H$
Alcohol-$(PO)_x$-$(EO)_y$-benzyl	Triton® DF-12 $C_{8-10}(PO)_2(EO)_{13}$-benzyl
Alcohol-$(EO)_x$-$(BuO)_y$H	Plurafac® LF-221 $C_{10-12}(EO)_{9.5}(BuO)_{1-2}$
Alcohol-$(EO)_x$-alkyl	Dehypon® Lt-104 $C_{16-18}(EO)_{12}CH_2OC_4H_9$
Alcohol-$(EO)_x$-benzyl	Triton® DF-18 $C_{14-16}(EO)_{16}$-benzyl

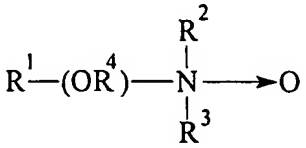
a NMR analysis
AP = alkylphenoxy
EO = ethylene oxide
PO = propylene oxide
BuO = butylene oxide

Triton® is a registered trade name of Union Carbide Chemical & Plastics Co.
Surfonic® is a registered trade name of Texaco Chemical Co.
Poly-Tergent® is a registered trade name of Olin Corporation.
Plurafac® is a registered trade name of BASF Corporation.
Dehypon® is a registered trade name of Henkel Corporation.

Semi-Polar Nonionic Surfactants

The semi-polar type of nonionic surface active agents are another class of nonionic surfactant useful in compositions of the present invention. Generally, semi-polar nonionics are high foamers and foam stabilizers which make their application in CIP systems limited. However, within compositional embodiments of this invention designed for high foam cleaning methodology, such as facility cleaning which often employs detersive solutions dispensed onto surfaces as a foam, semi-polar nonionics would have immediate utility. The semi-polar nonionic surfactants include the amine oxides, phosphine oxides, sulfoxides and their alkoxylated derivatives.

8. Amine oxides are tertiary amine oxides corresponding to the general formula:

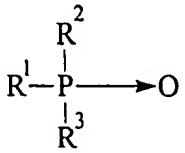


wherein the arrow is a conventional representation of a semi-polar bond; and, R^1, R^2, and R^3 may be aliphatic, aromatic, heterocyclic, alicyclic, or combinations thereof. Generally, for amine oxides of detergent interest, R^1 is an alkyl radical of from about 8 to about 24 carbon atoms; R^2 and R^3 are selected from the group consisting of alkyl or hydroxyalkyl of 1-3 carbon atoms and mixtures thereof; R^4 is an alkaline or a hydroxyalkylene group containing 2 to 3 carbon atoms; and n ranges from 0 to about 20.

Useful water soluble amine oxide surfactants are selected from the coconut or tallow alkyl di-(lower alkyl) amine oxides, specific examples of which are dodecyldimethylamine oxide, tridecyldimethylamine oxide, etradecyldimethylamine oxide, pentadecyldimethylamine oxide, hexadecyldimethylamine oxide, heptadecyldimethylamine oxide, octadecyldimethylaine oxide, dodecyldipropylamine oxide, tetradecyldipropylamine oxide, hexadecyldipropylamine oxide, tetradecyldibutylamine oxide,

octadecyldibutylamine oxide, bis(2-hydroxyethyl)dodecylamine oxide, bis(2-hydroxyethyl)-3-dodecoxy-1-hydroxypropylamine oxide, dimethyl-(2-hydroxydodecyl)amine oxide, 3,6,9-trioctadecyldimethylamine oxide and 3-dodecoxy-2-hydroxypropyldi-(2-hydroxyethyl)amine oxide.

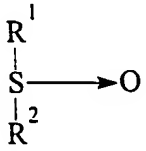
Useful semi-polar nonionic surfactants also include the water soluble phosphine oxides having the following structure:



wherein the arrow is a conventional representation of a semi-polar bond; and, R^1 is an alkyl, alkenyl or hydroxyalkyl moiety ranging from 10 to about 24 carbon atoms in chain length; and, R^2 and R^3 are each alkyl moieties separately selected from alkyl or hydroxyalkyl groups containing 1 to 3 carbon atoms.

Examples of useful phosphine oxides include dimethyldecylphosphine oxide, dimethyltetradecylphosphine oxide, methylethyltetradecylphosphone oxide, dimethylhexadecylphosphine oxide, diethyl-2-hydroxyoctyldecylphosphine oxide, bis(2-hydroxyethyl)dodecylphosphine oxide, and bis(hydroxymethyl)tetradecylphosphine oxide.

Semi-polar nonionic surfactants useful herein also include the water soluble sulfoxide compounds which have the structure:



wherein the arrow is a conventional representation of a semi-polar bond; and, R^1 is an alkyl or hydroxyalkyl moiety of about 8 to about 28 carbon atoms, from 0 to about 5 ether linkages and from 0 to about 2 hydroxyl substituents; and R^2 is an

alkyl moiety consisting of alkyl and hydroxyalkyl groups having 1 to 3 carbon atoms.

Useful examples of these sulfoxides include dodecyl methyl sulfoxide; 3-hydroxy tridecyl methyl sulfoxide; 3-methoxy tridecyl methyl sulfoxide; and 3-hydroxy-4-dodecoxybutyl methyl sulfoxide.

Anionic Surfactants

Also useful in the present invention are surface active substances which are categorized as anionics because the charge on the hydrophobe is negative; or surfactants in which the hydrophobic section of the molecule carries no charge unless the pH is elevated to neutrality or above (e.g. carboxylic acids). Carboxylate, sulfonate, sulfate and phosphate are the polar (hydrophilic) solubilizing groups found in anionic surfactants. Of the cations (counterions) associated with these polar groups, sodium, lithium and potassium impart water solubility; ammonium and substituted ammonium ions provide both water and oil solubility; and, calcium, barium, and magnesium promote oil solubility.

As those skilled in the art understand, anionics are excellent detersive surfactants and are therefore, favored additions to heavy duty detergent compositions. Generally, however, anionics have high foam profiles which limit their use alone or at high concentration levels in cleaning systems such as CIP circuits that require strict foam control. However, anionics are very useful additives to preferred compositions of the present invention; at low percentages or in cooperation with a low foaming nonionic or defoam agent for application in CIP and like foam controlled cleaning regimens; and, at higher concentrations in detergent compositions designed to yield foaming detersive solutions. Certainly, anionic surfactants are preferred ingredients in various embodiments of the present invention which incorporate foam for dispensing and utility -- for example, clinging foams used for general facility cleaning.

Further, anionic surface active compounds are useful to impart special chemical or physical properties other than detergency within the composition. Anionics can be employed as gelling agents or as part of a gelling or thickening system. Anionics are excellent solubilizers and can be used for hydrotropic affect

and cloud point control. Anionics can also serve as the solidifier for solid product forms of the invention, and so forth.

The majority of large volume commercial anionic surfactants can be subdivided into five major chemical classes and additional sub-groups: (taken from "Surfactant Encyclopedia", Cosmetics & Toiletries, Vol. 104 (2) 71-86 (1989); and incorporated herein by reference).

A. Acylamino acids (and salts)
    1. Acylgluamates
    2. Acyl peptides
    3. Sarcosinates
    4. Taurates
B. Carboxylic acids (and salts)
    1. Alkanoic acids (and alkanoates)
    2. Ester carboxylic acids
    3. Ether carboxylic acids
C. Phosphoric acid esters (and salts)
D. Sulfonic acids (and salts)
    1. Acyl isethionates
    2. Alkylaryl sulfonates
    3. Alkyl sulfonates
    4. Sulfosuccinates
E. Sulfuric acid esters (and salts)
    1. Alkyl ether sulfates
    2. Alkyl sulfates

It should be noted that certain of these anionic surfactants may be incompatible with the enzymes incorporated into the present invention. As example, the acyl-amino acids and salts may be incompatible with proteolytic enzymes because of their peptide structure.

Examples of suitable synthetic, water soluble anionic detergent compounds are the ammonium and substituted ammonium (such as mono-, di- and triethanolamine) and alkali metal (such as sodium, lithium and potassium) salts of

the alkyl mononuclear aromatic sulfonates such as the alkyl benzene sulfonates containing from about 5 to about 18 carbon atoms in the alkyl group in a straight or branched chain, e.g., the salts of alkyl benzene sulfonates or of alkyl toluene, xylene, cumene and phenol sulfonates; alkyl naphthalene sulfonate, diamyl naphthalene sulfonate, and dinonyl naphthalene sulfonate and alkoxylated derivatives. Other anionic detergents are the olefin sulfonates, including long chain alkene sulfonates, long chain hydroxyalkane sulfonates or mixtures of alkenesulfonates and hydroxyalkane-sulfonates. Also included are the alkyl sulfates, alkyl poly(ethyleneoxy) ether sulfates and aromatic poly(ethyleneoxy) sulfates such as the sulfates or condensation products of ethylene oxide and nonyl phenol (usually having 1 to 6 oxyethylene groups per molecule. The particular salts will be suitably selected depending upon the particular formulation and the needs therein.

The most preferred anionic surfactants for the most preferred embodiment of the invention are the linear or branched alkali metal mono and/or di-(C_{6-14})alkyl diphenyl oxide mono and/or disulfonates, commercially available from Dow Chemical, for example as DOWFAX® 2A-1, and DOWFAX® C6L.

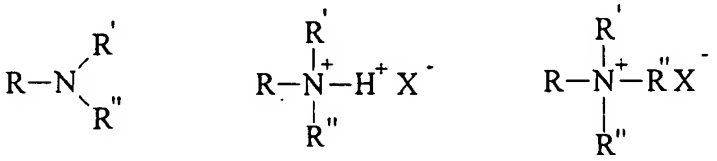
Cationic Surfactants

Surface active substances are classified as cationic if the charge on the hydrotrope portion of the molecule is positive. Surfactants in which the hydrotrope carries no charge unless the pH is lowered close to neutrality or lower are also included in this group (e.g. alkyl amines). In theory, cationic surfactants may be synthesized from any combination of elements containing an "onium" structure RnX+Y- and could include compounds other than nitrogen (ammonium) such as phosphorus (phosphonium) and sulfur (sulfonium). In practice, the cationic surfactant field is dominated by nitrogen containing compounds, probably because synthetic routes to nitrogenous cationics are simple and straightforward and give high yields of product, e.g. they are less expensive.

Cationic surfactants refer to compounds containing at least one long carbon chain hydrophobic group and at least one positively charge nitrogen. The long carbon chain group may be attached directly to the nitrogen atom by simple substitution; or more preferably indirectly by a bridging functional group or groups

in so-called interrupted alkylamines and amido amines which make the molecule more hydrophilic and hence more water dispersible, more easily water solubilized by co-surfactant mixtures, or water soluble. For increased water solubility, additional primary, secondary or tertiary amino groups can be introduced or the amino nitrogen can be quaternized with low molecular weight alkyl groups. further, the nitrogen can be a member of branched or straight chain moiety of varying degrees of unsaturation; or, of a saturated or unsaturated heterocyclic ring. In addition, cationic surfactants may contain complex linkages having more than one cationic nitrogen atom.

The surfactant compounds classified as amine oxides, amphoterics and zwitterions are themselves cationic in near neutral to acidic pH solutions and overlap surfactant classifications. Polyoxyethylated cationic surfactants behave like nonionic surfactants in alkaline solution and like cationic surfactants in acidic solution. The simplest cationic amines, amine salts and quaternary ammonium compounds can be schematically drawn thus:



R represents a long alkyl chain, R', R", and R"' may be either long alkyl chains or smaller alkyl or aryl groups or hydrogen and X represents an anion. Only the amine salts and quaternary ammonium compounds are of practical use in this invention because of water solubility.

11. The majority of large volume commercial cationic surfactants can be subdivided into four major classes and additional sub-groups: (taken from "Surfactant Encyclopedia", Cosmetics & Toiletries, Vol. 104 (2) 86-96 (1989); and incorporated herein by reference.

A. Alkylamines (and salts)

B. Alkyl imidazolines

C. Ethoxylated amines

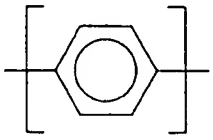
D. Quaternaries

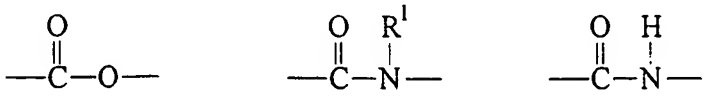
1. Alkylbenzyldimethylammonium salts
2. Alkyl benzene salts
3. Heterocyclic ammonium salts
4. Tetra alkylammonium salts

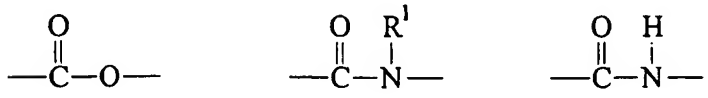
As utilized in this invention, cationics are specialty surfactants incorporated for specific effect; for example, detergency in compositions of or below neutral pH; antimicrobial efficacy; thickening or gelling in cooperation with other agents; and so forth.

The cationic surfactants useful in the compositions of the present invention have the formula $R^1{}_m R^2{}_x Y_L Z$ wherein each R^1 is an organic group containing a straight or

branched alkyl or alkenyl group optionally substituted with up to three phenyl or hydroxy groups and optionally interrupted by up to four structures selected from the following group:



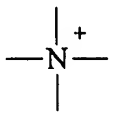


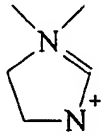


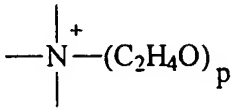
isomers and mixtures thereof, and which contains from about 8 to 22 carbon atoms. The R^1 groups may additionally contain up to 12 ethoxy groups. m is a number from 1 to 3. No more than one R^1 group in a molecule can have 16 or more carbon atoms when m is 2 or more than 12 carbon atoms when m is 3. Each R^2 is an alkyl or hydroxyalkyl group containing from 1 to 4 carbon atoms or a benzyl group with no

more than one R^2 in a molecule being benzyl, and x is a number from 0 to 11, preferably from 0 to 6. The remainder of any carbon atom positions on the Y group are filled by hydrogens.

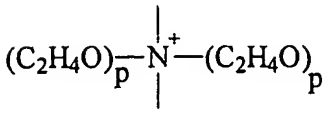
Y is selected from the group consisting of, but not limited to:



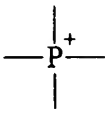


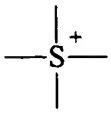


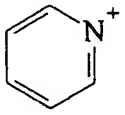
p=about 1 to 12

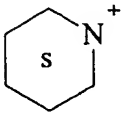


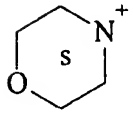
p=about 1 to 12











and mixtures thereof.

L is 1 or 2, with the Y groups being separated by a moiety selected from R^1 and R^2 analogs (preferably alkylene or alkenylene) having from 1 to about 22 carbon atoms and two free carbon single bonds when L is 2. Z is a water soluble anion, such as a halide, sulfate, methylsulfate, hydroxide, or nitrate anion, particularly preferred being chloride, bromide, iodide, sulfate or methyl sulfate anions, in a number to give electrical neutrality of the cationic component.

Amphoteric Surfactants

Amphoteric surfactants contain both a basic and an acidic hydrophilic group and an organic hydrophobic group. These ionic entities may be any of anionic or cationic groups described in the preceding sections. A basic nitrogen and an acidic carboxylate group are the predominant functional groups, although in a few structures, sulfonate, sulfate, phosphonate or phosphate provide the negative charge.

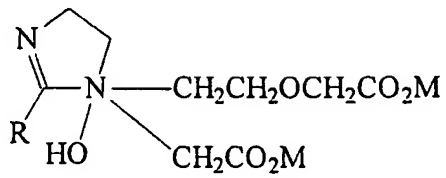
Ampholytic surfactants can be broadly described as derivatives of aliphatic secondary and tertiary amines, in which the aliphatic radical may be straight chain or branched and wherein one of the aliphatic substituents contains from about 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfo, sulfato, phosphato, or phosphono. Amphoteric surfactants are subdivided into two major classes: (taken from "Surfactant Encyclopedia" Cosmetics & Toiletries, Vol. 104 (2) 69-71 (1989).

A. Acyl/dialkyl ethylenediamine derivatives (2-alkyl hydroxyethyl imidazoline derivatives) (and salts)

B. N-alkylamino acids (and salts)

2-alkyl hydroxyethyl imidazoline is synthesized by condensation and ring closure of a long chain carboxylic acid (or a derivative) with dialkyl ethylenediamine. Commercial amphoteric surfactants are derivatized by subsequent hydrolysis and ring-opening of the imidazoline ring by alkylation -- for example with chloroacetic acid or ethyl acetate. During alkylation, one or two carboxy-alkyl groups react to form a tertiary amine and an ether linkage with differing alkylating agents yielding different tertiary amines.

Long chain imidazole derivatives having application in the present invention generally have the general formula:



wherein R is an acyclic hydrophobic group containing from about 8 to 18 carbon atoms and M is a cation to neutralize the charge of the anion, generally sodium.

Commercially prominent imidazoline-derived amphoterics include for example:

Cocoamphopropionate, Cocoamphocarboxy-propionate, Cocoamphoglycinate, Cocoamphocarboxy-glycinate, Cocoamphopropyl-sulfonate, and Cocoamphocarboxy-propionic acid.

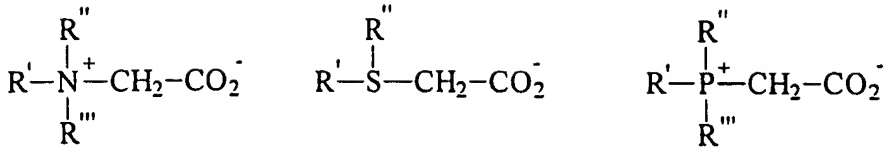
The carboxymethylated compounds (glycinates) listed above frequently are called betaines. Betaines are a special class of amphoteric discussed in the section entitled, Zwitterion Surfactants.

Long chain N-alkylamino acids are readily prepared by reaction RNH_2($R=C_8$-C_{18}) fatty amines with halogenated carboxylic acids. Alkylation of the primary amino groups of an amino acids leads to secondary and tertiary amines. Alkyl substituents may have additional amino groups that provide more than one reactive nitrogen center. Most commercial N-alkylamine acids are alkyl derivatives of beta-alanine or beta-N(2-carboxyethyl) alanine.

Examples of commercial N-alkylamino acid ampholytes having application in this invention include alkyl beta-amino dipropionates, $RN(C_2H_4COOM)_2$ and $RNHC_2H_4COOM$. R is an acyclic hydrophobic group containing from about 8 to about 18 carbon atoms, and M is a cation to neutralize the charge of the anion.

Zwitterionic Surfactants

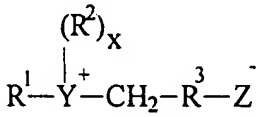
The presence of a positive charged quaternary ammonium or, in some cases, of a sulfonium or phosphonium ion; and of a negative charged carboxyl group within a compound of aliphatic derivative generally of betaine structure:



yields an amphoteric of special character termed a zwitterion. These amphoterics contain cationic and anionic groups which ionize to a nearly equal degree in the isoelectric region of the molecule and develop strong"inner-salt" attraction between positive-negative charge centers. As a result, surfactant betaines do not exhibit strong cationic or anionic characters at pH extremes nor do they show reduced water solubility in their isoelectric range. Unlike "external" quaternary ammonium salts, betaines are compatible with anionics.

Zwitterionic synthetic surfactants useful in the present invention can be broadly described as derivatives of aliphatic quaternary ammonium, phosphonium, and sulfonium compounds, in which the aliphatic radicals can be straight chain or branched, and wherein one of the aliphatic substituents contains from 8 to 18 carbon atoms and one contains an anionic water solubilizing group, e.g., carboxy, sulfonate, sulfate, phosphate, or phosphonate.

A general formula for these compounds is:



wherein R^1 contains an alkyl, alkenyl, or hydroxyalkyl radical of from 8 to 18 carbon atoms having from 0 to 10 ethylene oxide moieties and from 0 to 1 glyceryl moiety; Y is selected from the group consisting of nitrogen, phosphorus, and sulfur atoms; R^2 is an alkyl or monohydroxy alkyl group containing 1 to 3 carbon atoms; x is 1 when Y is a sulfur atom and 2 when Y is a nitrogen or phosphorus atom, R^3 is an alkylene or hydroxy alkylene or hydroxy alkylene of from 1 to 4 carbon atoms and Z

is a radical selected from the group consisting of caboxylate, sulfonate, sulfate, phosphonate, and phosphate groups.

Examples include:

4-[N,N-di(2-hydroxyethyl)-N-octadecylammonio]-butane-1 -carboxylate;

5-[S-3-hydroxypropyl-S-hexadecylsulfonio]-3-hydroxypentane-1-sulfate;

3-[P,P-diethyl-P-3,6,9-trioxatetracosanephosphonio]-2-hydroxypropane-1-phosphate;

3-[N,N-dipropyl-N-3-dodecoxy-2-hydroxypropyl-ammonio]-propane-1-phosphonate;

3-(N,N-dimethyl-N-hexadecylammonio)-propane-1-sulfonate;

3-(N,N-dimethyl-N-hexadecylammonio)-2-hydroxy-propane-1-sulfonate;

4-[N,N-di(2(2-hydroxyethyl)-N(2-hydroxydodecyl)ammonio]-butane-1-carboxylate;

3-[S-ethyl-S-(3-dodecoxy-2-hydroxypropyl)sulfonio]-propane-1-phosphate;

3-[P,P-dimethyl-P-dodecylphosphonio]-propane-1-phosphonate; and

S[N,N-di(3-hydroxypropyl)-N-hexadecylammonio]-2-hydroxy-pentane-1-sulfate.

The alkyl groups contained in said detergent surfactants can be straight or branched and saturated or unsaturated.

The nonionic and anionic surfactants enumerated above can be used singly or in combination in the practice and utility of the present invention. The semi-polar nonionic, cationic, amphoteric and zwitterionic surfactants generally are employed in combination with nonionics or anionics. The above examples are merely specific illustrations of the numerous surfactants which can find application within the scope of this invention. The foregoing organic surfactant compounds can be formulated into any of the several commercially desirable composition forms of this invention having disclosed utility. Said compositions are cleaning treatments for food soiled surfaces in concentrated form which, when dispensed or dissolved in water, properly diluted by a proportionating device, and delivered to the target surfaces as a solution, gel or foam will provide cleaning. Said cleaning treatments consisting of one

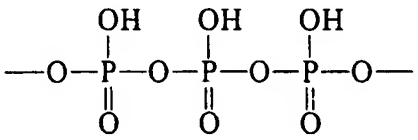
product; or, involving a two product system wherein proportions of each are utilized. Said product being concentrates of liquid or emulsion; solid, tablet, or encapsulate; powder or particulate; gel or paste; and slurry or mull.

Solidifying Agents

Solidifying agents are used in the claimed invention in order to convert the liquid detergent premix into a solid. Borate can function as a solidifying agent within the present invention. Additional solidifying agents can be drawn from the the group comprised of carbonates, bicarbonates, sulfates and urea.

Sequestrants

In order to soften or treat water, prevent the formation of precipitates or other salts, the composition of the present invention generally comprises components known as chelating agents, builders or sequestrants. Generally, sequestrants are those molecules capable of complexing or coordinating the metal ions commonly found in service water and thereby preventing the metal ions from interfering with the functioning of detersive components within the composition. Any number of sequestrants may be used in accordance with the invention. Representative sequestrants include salts of amino carboxylic acids, phosphonic acid salts, water soluble acrylic polymers, among others. The molecular weight (Mw) of these polymeric materials is about 200-8000, preferably 4000-6000. The term "condensed phosphate" indicates a material having at least one group according to the formula:



wherein the empty bonds are directed to other phosphate groups, cations, etc. which can be part of a linear, condensed or cyclic phosphate composition.

Compounds with phosphate moieties useful as sequestrants are alkali metal condensed phosphates, cyclic phosphates, organo phosphonic acids and organo phosphonic acid salts. Useful condensed phosphates include alkali metal

pyrophosphate, an alkali metal polyphosphate such as sodium tripolyphosphate (STPP) available in a variety of particle sizes. Useful organo phosphonic acids include, mono, di, tri and tetra-phosphonic acids which can also contain groups capable of forming anions under alkaline conditions such as carboxy, hydroxy, thio and the like.

The tendency of the condensed phosphate materials to revert can be controlled by using a condensed phosphate that reduces the impact of caustic and water on the sequestrant material. Such effects can be reduced by using an effective particle size sequestrant and by using barrier technologies.

The inorganic condensed phosphate can also be combined with an organic carboxylate, phosphonate, phosphonic acid or phosphonic acid salt. The organic materials can aid in sequestering hardness ions in cleaning processes. Suitable amino carboxylic acid chelating agents include N-hydroxyethyliminodiacetic acid, nitrilotriacetic acid (NTA), ethylenediaminetetraacetic acid (EDTA), N-hydroxyethyl-ethylenediaminetriacetic acid (HEDTA), and diethylenetriaminepentaacetic acid (DTPA). When used, these amino carboxylic acids are generally present in concentrations ranging from about 1 wt-% to 50 wt-%, preferably from about 2 wt-% to 45 wt-%, and most preferably from about 3 wt-% to 40 wt-%.

Other suitable sequestrants include water soluble acrylic polymers having pendant $-CO_2^{-1}$ groups, used to condition the wash solutions under end use conditions. Such polymers include polyacrylic acid, polymethacrylic acid, acrylic acid-methacrylic acid copolymers, acrylic acid-itaconic acid copolymers, hydrolyzed polyacrylamide, hydrolyzed methacrylamide, hydrolyzed acrylamide-methacrylamide copolymers, hydrolyzed polyacrylonitrile, hydrolyzed polymethacrylonitrile, hydrolyzed acrylonitrile methacrylonitrile copolymers, or mixtures thereof. Water soluble salts or partial salts of these polymers such as their respective alkali metal (for example, sodium or potassium) or ammonium salts can also be used. The number average molecular weight of the polymers is from about 4000 to about 12,000. Preferred polymers include polyacrylic acid, the partial sodium salts of polyacrylic acid or sodium polyacrylate having an average molecular weight within the range of 4000 to 8000. These acrylic polymers are generally

useful in concentrations ranging from about 0.5 wt-% to 20 wt-%, preferably from about 1 to 10, and most preferably from about 1 to 5.

Also useful are phosphonic acids are 1-hydroxyethane-1,1-diphosphonic acid; aminotri(methylenephosphonic acid); aminotri -(methylenephosphonate), sodium salt 2-hydroxy ethyl- iminobis(methylenephosphonic acid); diethylenetriaminepenta(methylenephosphonic acid);diethylene-triamine-penta(methylenephosphonate) sodium salt; hexamethylenediamine-(tetramethylenephosphonate), potassium salt; bis(hexamethylene) triamine(pentamethylenephosphonic acid) $(HO_2)POCH_2N[(CH_2)_6N[CH_2PO(OH)_2]_2]_2$; and phosphorus acid H_3PO_3. The preferred phosphonate is aminotrimethylenephosphonic acid or salts thereof combined optionally with diethylenetriaminepenta(methylenephosphonic acid). When used as a sequestrant in the invention, phosphonic acids or salts are present in a concentration ranging from about 0.25 to 25 wt-%, preferably from about 1 to 20 wt-%, and most preferably from about 1 to 18 wt-% based on the solid detergent.

Detailed Discussion of the Figure

The Figure shows data regarding the stability of the enzyme activity in the solid block materials. Each preparation should be compared to the enzyme control represented by the dashed line. Certain compositions. Examples 5, 6, 7, 8 and 9 all have superior enzyme activity stability when compared to the enzyme material alone. Such stability is present over twelve days under comparatively severe conditions.

Method of use

This refers to a cleaning method whereby the cleaning solution(s) is (are) pumped through the processing equipment as it stands in place. No disassembly of the processing equipment is required.

In the preferred embodiment of the present invention, the product is dissolved by spraying water in a solid dispenser and delivered to a sump or directly to use solution tank, from which the use solution is pumped to where cleaning is needed. The use concentration is typically about 0.1 % in aqueous solution. The pH

is about 9.0 to 10 and the temperature is between 130°F and 150°F (54.4 °C to 65.6 °C).

In any method of use, control over the concentration of the enzyme cleaner in the aqueous solution must be maintained. We have discovered that the conductivity of the ionic species in the aqueous solution (sodium, potassium, borate, etc. ions) can be used to control overall concentration of the detergent components including the surfactants, enzymes and other non-conductive materials. We have found that by using either DC or AC conductivity in measurements of the use solution that a spray on dispenser can be used to deliver an aqueous concentrate to maintain the use solution at an appropriate concentration of enzyme surfactant and other components. The conductivity of the use solution is measured using an electrical conductivity measurement means. As the conductivity of the use solution drops, typically the concentration of the enzyme, surfactant and other active ingredients in the use solution also is reduced proportionally. The use solution can be replenished of enzyme surfactant and other actives by introducing an aqueous concentrate made by spraying water onto the solid block detergent of the invention for a period of time sufficient to dispense an adequate amount of the detergent into the use solution. As the solid block containing the enzyme surfactant and other active components is dissolved by the water spray, the ionizable inorganic materials are also dispensed. By monitoring the conductivity created by the ionizable materials in the aqueous solution, the concentration of the enzyme component and other surfactants and other ingredients can also be controlled quite closely. Typically, the conductivity of the use solution is maintained between about 500 and 800 μsiemens/cm to provide an adequate concentration of enzyme, surfactant and other active ingredients.

Although measurements of conductivity have long been used as a means of investigating the properties of electrolytes in solution, such as dissociation, activity, formation of complexes, and hydrolysis, such measurements also provide the basis for instrumentation used in industry to detect the ionic contamination of water and to determine the concentration of simple electrolytic solutions (see Van Nostrand's Scientific Encyclopedia, 6th Edition, Volume I, pp 1056-1058). In this reference, the term electrolytic conductivity has been applied almost exclusively to water solutions of electrolytes in which the mechanism of electrical current transfer is

dependent on ions. Solid and fused salts, however, also exhibit electrolytic conductivity.

Electrolytic conductivity (specific conductance) is defined as the electrical conductance of a unit cube of electrolytic solution. It is expressed in the same units as electrical conductivity, i.e., reciprocal ohms per unit length. Most commonly we find conductivity units of:

Mhos/cm, siemens/cm, microsiemens/cm ($\mu S\text{-}cm^{-1}$) and siemens/meter

(1mho/cm = 1 siemens/cm = 100 siemens/meter)

Typically the conductivity increases to a maximum value and then decreases with increasing concentration. Sometimes an additional point of inflection may occur. The conductivity of salt solutions typically increase with temperature. Pure water changes somewhat more with changes in temperature while strong acids and bases change somewhat less. From the foregoing discussion it can be seen that the value of a conductivity measurement is useless without knowledge of the temperature at which the measurement was made.

Electrolytic conductivity is most often measured by placing electrodes in contact with the electrolytic solution which is contained in such a way that the measured electrical conductance between the electrodes can be related to the conductivity of the solution. A conductivity cell commonly comprises an enclosure made of electrically insulating material such as glass or plastic which holds a portion of the solution and accommodates the two electrodes. The cell constant of such a device is then used to relate the measured electrical conductance between the electrodes to the actual electrolytic conductivity. Two electrodes 1 centimeter square located on opposite interior faces of a hollow cube 1 centimeter on an edge would have a cell constant of 1/cm, and a measured conductance of 0.005 mhos/cm (0.5 siemens/meter) at 25°C.

If the electrical conductance between the electrodes is measured with direct current, the resulting electrolysis and gas evolution can interfere with the current passage and changes the composition of the solution. Alternating current measurements greatly reduces these interfering factors, and finds wide use in such

measurements. Properly designed inductive AC conductivity cells operated at appropriate alternating current frequencies obey Ohm's law since the current through the cell is proportional to the applied voltage and the conductivity of the electrolytic solution. Alternating current Wheatstone bridges and conductance meters make up the most widely used instrumentation accepted for electrolytic conductivity measurements. Changes in solution temperature change bridge characteristics similarly, thereby allowing the bridge to remain balanced except for actual changes in solution concentration. Conductivity meters generally apply a constant alternating voltage across the electrodes and respond to the resulting flow of current, which is proportional to the conductivity of the solution. Means of automatic temperature compensation are also included in such circuitry.

Measurements of electrolytic conductivity by means of electrical induction can be done without the use of contacting electrodes. Such measurements are made by inducing an alternating current in an electrolyte by use of a coil of wire. The magnitude of the induced current is proportional to the conductivity of the electrolyte. Current is caused to flow in a closed circular path through the electrolyte by a first coil of wire wound on a toroidal core of magnetic material. The magnitude of the current and hence the conductivity is measured by a second similar coil.

A typical laboratory-type DC conductivity cell, which employs two platinized platinum electrodes contained in an open-bottom cylindrical chamber formed from pyrex glass. This cell has a cell constant of 0.5/cm and is intended for use in measuring the conductivity of distilled water and other dilute solutions used in the laboratory. This kind of cell is dipped into an open-topped container containing the sample to be measured. Wide use is made in the laboratory of conductivity cells of this type in ascertaining water quality and in screening samples to be titrated or further analyzed by other means. A large variety of conductivity cells are available for use including DC and AC cells, electroless cells and others.

Examples

In order to test the stability of the claimed invention, various formulations were tested. These formulations are disclosed in the following table:

SOLID ENZYME CLEANER FORMULATIONS

INGREDIENTS	1	2	3	4	5	6	7	8	9	10
Purafect 4000L (protease)	5.00	5.00	5.00	5.00	5.00	5.00	5.00	5.00	2.70	6.25
Surfonic Lf41 (alcohol alkoxylates nonionic)									10.70	25.00
Dry Milk	5.00	5.00			5.00	5.00				
DI-H20	16.86	16.86	16.86	16.86	15.00	15.00	15.00	15.00		27.50
Propylene glycol										12.25
Potassium naxonate (cumene sulfonate)										26.00
Triethanol amine										2.00
Borax $Na_2B_4O_6$	3.14	12.56	3.14	12.56	65.00	35.00	70.00	60.00	30.00	
Dense Ash	60.00	50.58	65.00	55.58					29.00	
Lactose										
Sucrose	10.00	10.00	10.00	10.00	10.00	10.00	10.00	20.00	10.00	
Polyacrylic acid (50%)									11.90	
Sodium sulfate						30.00				
Sodium metabisulfite									1.00	1.00
Potassium hydroxide (45%)									4.70	
Total	100.00	100.00	100.00	100.00	100.00		100.00	100.00	100.00	100.00

The specific test results are listed in the table below, and are shown graphically in figure 1 as well:

SOLID PRODUCT STABILTY-FORMULATION STUDY

SAMPLE Formulation	Percent of Act. Lost During Production	2/3 Day/120F Residual Enzyme Activity	4 Day/120F Residual Enzyme Activity (% of Initial)	12 Day/120F Residual Enzyme Activity *% of Initial)
1	21	99	30	0
2	21	109	81	25
3	41	77	16	0
4	34	83	52	7.5
5	11	111	113	110
6	18	106	117	114
7	34	117	96	118
8	24	99	104	99
9	15	95	87	86

Further, the conductivity of various solutions was tested. The results are given in the following table:

CONDUCTIVITY BASED DOSING CONTROL

Use of an electrolyte like a sodium allows conductivity to be used for dosing control of enzyme and surfactant as well.

CONDUCTIVITY

Material	$\mu S\text{-}cm^{-1}$ (μsiemens/cm)
600 ppm of Formulation 9	453
Formulation 9 @ 800 ppm	590
Formulation 9 @ 900 ppm	649
Formulation 9 @ 1000 ppm	714
Formulation 9 @ 2000 ppm	1,345
Formulation 9 @ 1000 ppm with +0.5% milk	773
Formulation 9 @ 1000 ppm with +1.0% milk	751
Formulation 9 @ 1000 ppm with +2.0%	861
745 ppm KCL	1,380
Deionized water	0.672
Typical City water	200-300

Conductivity probes (inductive or electride) can be used to monitor the concentration of enzyme in washing solutions when dispensed from a spray on dispenser. The use of an electrolyte material in the detergent can increase the conductivity of deionized water (at about 1 $\mu S\text{-}cm^{-1}$) to an adequate conductivity or for typical service water from municipal utilities that can range from 100 to 300 $\mu S\text{-}cm^{-1}$. Since detergent materials are typically dispensed in city water, a substantial increase in conductivity is required to control enzyme concentration when dispensed in city water. Accordingly, a substantial difference in conductivity must be obtained from the dispensed material when compared to city water conductivity. Accordingly, a minimum conductivity of the wash solution is greater than about 300 μsemens/cm preferably greater than 400 μsemens/cm, most preferably greater than 450 μsemens/cm. Often the process can efficiently operate at conductivities that range greater than 650 μsemens/cm, greater than 700 μsemens/cm or greater than 1000 μsemens/cm. We have found that even in the

presence of substantial soil, that the conductivity of the enzyme cleaner is useful in controlling concentration. The material can be dispensed even in the presence of substantial milk concentration, a soil that can coat electrode surfaces and reduce efficiency.

The above specification, examples and data provide an enabling description of the manufacture and use of the composition of the invention. Since many embodiments of the invention can be made without departing from the spirit and scope of the invention, the invention resides in the claims hereinafter appended. All percentages in the claims are based on the detergent composition as a whole.

WE CLAIM:

1. A method for dispensing a solid block enzyme composition, with a spray-on dispenser, into a use locus, the method having control over enzyme concentration, the method comprising:

(a) positioning a solid block detergent proximate a water spray means, the detergent comprising an enzyme and an electrolyte, the spray means capable of creating an aqueous concentrate when spraying the block detergent with water and directing the aqueous concentrate into a volume of aqueous cleaner into a use locus; and

(b) maintaining an effective concentration of enzyme by causing the spray on dispenser to create the concentrate and control the enzyme concentration by maintaining the conductivity of the volume of aqueous cleaner above a preselected minimum conductivity.

2. The method of claim 1 wherein the minimum conductivity comprises about 300 $\mu S\text{-}cm^{-1}$.

3. The method of claim 1 wherein the minimum conductivity comprises about 400 $\mu S\text{-}cm^{-1}$.

4. The method of claim 1 wherein the minimum conductivity comprises about 500 $\mu S\text{-}cm^{-1}$.

5. The method of claim 1 wherein the minimum conductivity comprises about 750 $\mu S\text{-}cm^{-1}$.

6. The method of claim 1 wherein the use locus comprises a clean-in-place system.

7. The method of claim 6 wherein the clean-in-place system is installed in a dairy.

8. A solid block enzyme containing cleaning composition comprising:

(a) about 0.1 to 50 wt.% of an enzyme cleaner composition; and

(b) an effective amount of a stabilizer composition comprising about 1 to 40 wt.% of an alkali metal borate;

wherein the detergent is formed in a container or by extrusion.

9. The composition of claim 8 wherein the enzyme comprises a protease.

10. The composition of claim 8 wherein the stabilizer composition further comprises a carbohydrate.

11. The composition of claim 8 wherein the carbohydrate comprises a monosaccharide comprising glucose, galactose, fructose or mixtures thereof.

12. The composition of claim 8 wherein the carbohydrate comprises a disaccharide comprising sucrose, lactose, maltose or mixtures thereof.

13. The composition of claim 8 wherein the cleaning composition additionally comprises an effective amount of a solidifying agent.

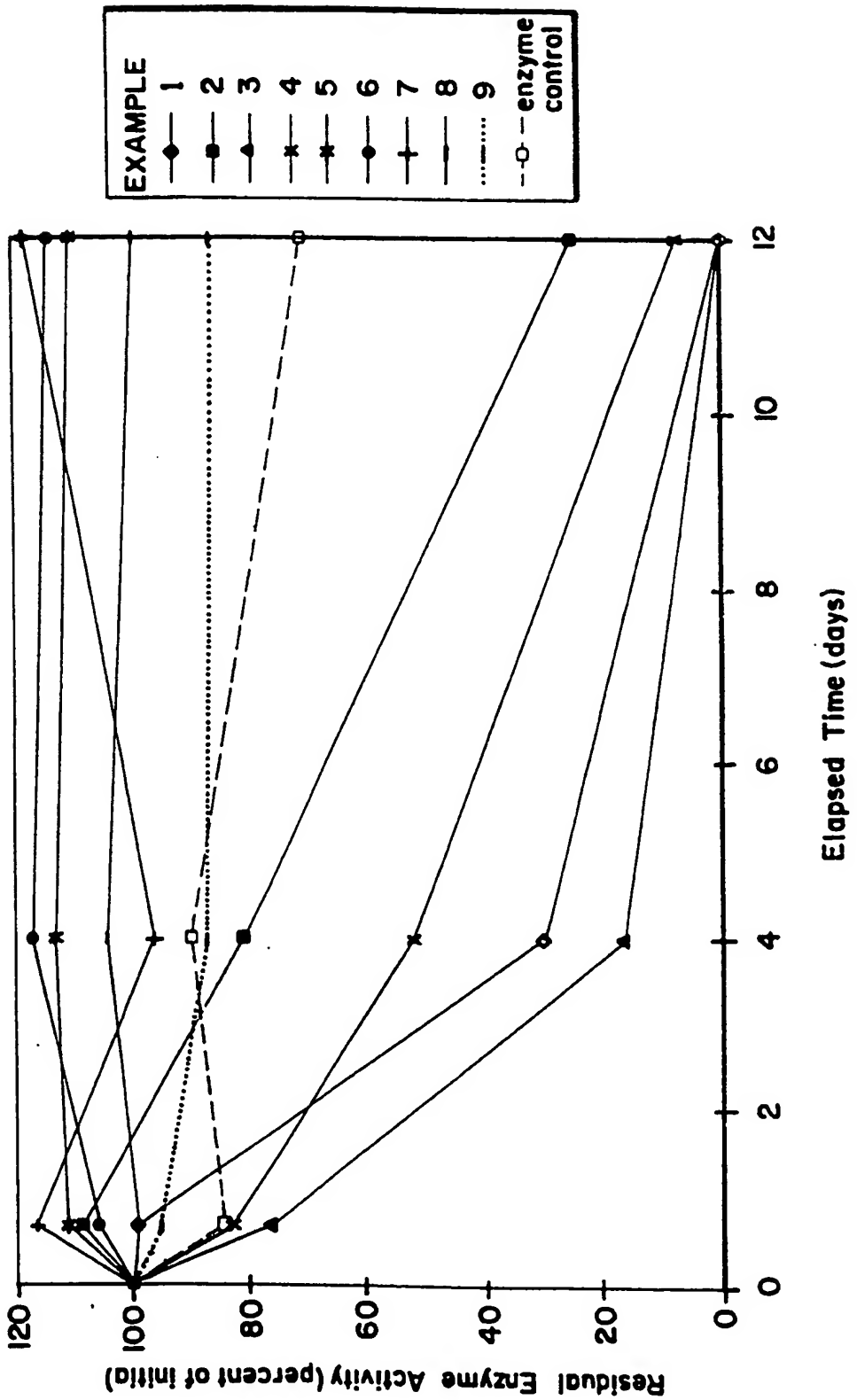
14. The composition of claim 13 wherein the solidifying agent comprises an alkali metal carbonate, an alkali metal bicarbonate or an alkali borate, or mixtures thereof.

15. The composition of claim 14 wherein the alkali borate is a disodium tetraborate in anhydrous, pentahydrate or decahydrate form or mixtures thereof.

16. The composition of claim 8 wherein the cleaning composition additionally comprises a surfactant, a sequestrant, an antioxidant, an antimicrobial agent, or an anticorrosion agent or mixtures thereof.

17. The composition of claim 8 wherein the solid enzyme containing detergent is in a rod, briquette or block form packaged in a bag, bucket or capsule, or shrink-wrapped.

18. The composition of claim 8 wherein the solid enzyme containing detergent is extruded and formed in a bucket.


EXAMPLE
1
2
3
4
5
6
7
8
9
enzyme control
Residual Enzyme Activity (percent of initial)
120
100
80
60
40
20
0
0
2
4
6
8
10
12
Elapsed Time (days)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/05748

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: C11D 3/386, C11D 17/00, A23C 7/02
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: C11D, B08B, A23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 9606910 A2 (ECOLAB INC.), 7 March 1996 (07.03.96) --	1-18
A	US 4858449 A (CHRIS F. LEHN), 22 August 1989 (22.08.89) --	1-7
X	GB 2271120 A (UNILEVER PLC), 6 April 1994 (06.04.94), claims 1-3, page 3, line 10 - line 11 --	8-18
A	EP 0501375 A1 (KAO CORPORATION), 2 Sept 1992 (02.09.92) --	8-18

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" erlier document but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 June 1999	23. 07. 99
Name and mailing address of the International Searching Authority European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel(+31-70)340-2040, Tx 31 651 epo nl, Fax(+31-70)340-3016	Authorized officer Telephone No.

Form PCT ISA 210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 99/05748

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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INTERNATIONAL SEARCH REPORT

Information on patent family members

01/06/99

International application No.
PCT/US 99/05748

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